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(54) **Water-absorbent resin and production process.**

(57) This invention relates to a water-absorbent resin of new, novel type obtained from polymerization of a water-soluble ethylenically unsaturated monomer followed by surface treatment and, in addition, a process for producing this resin.

The water-absorbent resin in this invention has average particle diameter in a specially defined range and a narrow range of particle distribution. And furthermore, since the particle surface is treated with crosslinking, a balance is very good among water absorption properties, for example, between water absorption capacity and water absorption rate, and between gel strength and suction force. This water-absorbent resin is takable a angle-lacking, non-sphere shape and in a case of this type of shape, it is superior in such handling properties as falling off from an basis material being hard.

Since the production process in the present invention comprises crosslinking treatment for the particle surface of a specially defined water-absorption polymer, the crosslinking is performed with good efficiency and, a water-absorption resin being superior in a balance among water absorption properties is obtainable with an economic advantage. This specially defined water-absorption polymer particle is obtained by polymerizing a water-soluble ethylenically unsaturated monomer in a process of reverse-phase suspension polymerization. In the production process of this invention, since the aqueous monomer solution is chosen from those in a specially defined viscosity range and then, dispersed and suspended by using a specially defined dispersing agent, a specially defined water-absorbent resin is easily obtainable wherein, not only the average particle diameter is controlled by adjusting the viscosity of an aqueous monomer solution, but also the particle diameter distribution resulted is narrow.

In this production process, the particle shape can be changed by changing up and down the viscocity of an

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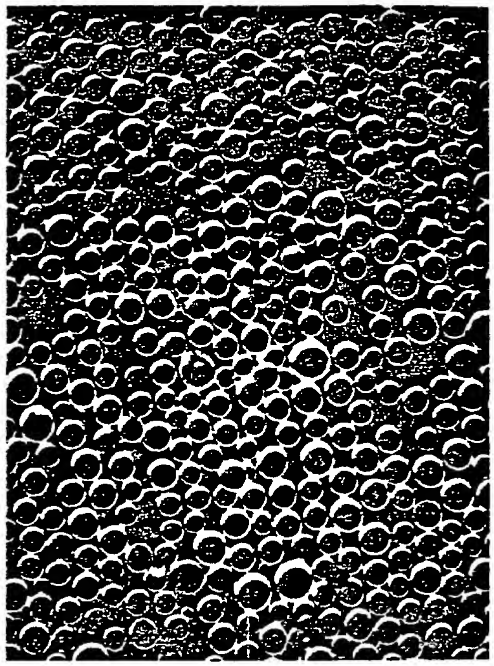
aqueous solution of monom r in the above-described specially defined range.

The water-absorbent resin in this invention, because it has the above-described properties, is preferably used for sanitary materials and the like.

Fig.1



WATER-ABSORBENT RESIN AND PRODUCTION PROCESS

BACKGROUND OF THE INVENTION

This invention relates to a water-absorbent resin and a process for producing this resin. In detail, it relates to a water-absorbent resin having average particle diameter in a specially defined range, narrow range of particle distribution, and a surface of uniformly improved quality and, in particular, being superior in water absorption capacity, water absorption rate, suction force, and gel strength etc., showing that water absorption properties are in good balance, showing that an amount of elution of water-soluble resin (hereinafter referred to as water-soluble component) is only small, and being very suitable as sanitary materials, and also, a process for producing the water-absorbent resin. Furthermore, this invention relates to a water-absorbent resin of a new, novel type showing angle-lacking, non-sphere, being superior in handling and treating, and having a surface of uniformly improved quality, and a process for producing the water-absorbent resin.

Hitherto, an attempt has been carried out to use a water-absorbent resin as an absorbent sanitary material for absorbing body fluids such as a sanitary cotton, a disposable diaper, and the like. There have been known, as water-absorbent resins for this purpose, a hydrolyzed starch-acrylonitrile graft polymer (Japanese Official Patent Gazette, showa 49-43395), a neutralized starch-acrylic acid graft polymer (Japanese Official Patent Provisional Publication, showa 51-125468), a saponified vinyl acetate-acrylic acid ester copolymer (Japanese Official Patent Provisional Publication, showa 52-14689), a hydrolyzed acrylonitrile or acrylamide copolymer (Japanese Official Patent Gazette, Showa 53-15959), and crosslinked products of these polymers, a crosslinked product of a partially neutralized polyacrylic acid (Japanese Official Patent Provisional Publication, Showa 55-84304) and others.

Incidentally, as properties to be wanted for water-absorbent resins, are cited high water absorption capacity, a water absorption rate, and high gel strength of water-contained swelling gel when the resins are coming in contact with aqueous liquid, and superior suction force to suck up water from a basic material containing aqueous liquid. These properties hitherto have been in a poor balance. That is, these properties are not in directly proportional relation, in particular, water absorption capacity and water absorption rate or gel strength and suction force are in reversely proportional relation, so that there has been found a trend that, as the water absorption capacity increases, other properties decrease. When some resins of a high water-absorbent capacity come in contact with aqueous liquid, aqueous liquid does not spread over the whole part of a water-absorbent resin and the resins form lumps, that is, what we call fish-eyes, so that an extreme lowering of a water absorption rate is observed. Also, in a case of that these water-absorbent resins are used for an absorption body of sanitary materials, the above-described water-soluble component being contained in the water-absorbent resins affects on the absorption capacity of an absorption body, liquid-spreading in a absorption body, and so on.

Especially, as the water-absorption capacity for a water-absorption resin increases, elution of a water-soluble component increases in amount, so that there has been found a problem that the resin can not properly used as sanitary materials.

As methods to improve the above-described properties with maintaining their good balance, there have been proposed methods to improve such properties as a water absorption rate etc. by crosslinking the surface of an obtained water-absorbent resin, without giving damage for water absorption capacity which the water-absorbent resin itself has. They are a method wherein a water-absorbent resin being dispersed in a hydrophilic organic solvent or a hydrophobic organic solvent in presence of water and undergoing to react in addition of a crosslinking agent (or its aqueous solution) (Japanese Official Patent Gazette, shouwa 61-48521 and 60-18690) and a method wherein a water-absorbent resin powder was mixed with a crosslinking agent or a liquid composition containing a crosslinking agent to treat with heat (Japanese Official Patent Provisional Publication, shouwa 58-180233, 59-189103, and 61-16903) and so on.

In these cases, of importance are uniform dispersion of a crosslinking agent over the surface of a water-absorbent resin and proper permeation into a neighborhood of the surface and, in addition, it is liked that the process is of advantage to industry. However, hitherto known methods have had problems in these points. That is, in the method wherein a water-absorbent resin being dispersed in a solvent and undergoing a crosslinking reaction, a large amount of solvent is required and so, its recovery process is of disadvantage to industry. Especially, in a case being carried out in a hydrophobic organic solvent, distribution of a crosslinking agent on the surface of a water-absorbent resin is apt to become ununiform, so that the

crossliking of surface becomes ununiform. In the other hand, the method wherein a water-absorbent resin is mixed with a liquid component containing a crossl nking agent and treated with heat, is of great advantage to industry, and however, in a cas of that particle diameter of a water-absorbent resin is small or distribution of particle diameter is broad, there was found a case that, though being affected on a treatment solution mixing with the water-absorbent resin powder, the powder meets together making a large lump (a fish-eye) and so, it is rather hard to crosslink uniformly the surface. Futhermore, though by doing these treatments such properties as water absorption rate and suction force are somewhat improved, but the improvement is still insufficient and, in particular, elution of a water-soluble component could not be prevented. Thus, has not yet found a method sufficiently satisfied in point of that various kinds of properties of a water-absorbent resin are improved maintaining good balance of properties.

BRIEF SUMMARY OF THE INVENTION

Under these circumstances, the first object of this invention is to provide a water-absorbent resin, wherein the average particle diameter being in a specially defined range, the particle diameter distribution being narrow, the surface being uniformly improved, and in particular, to provide a water-absorbent resin wherein the water absorption capacity, water absorption rate, suction force, and gel strength being superior and an amount of a water-soluble component being small, and a process for producing this resin.

The second object of this invention is to provide a water-absorbent resin wherein the shape being angle-lacking, non-sphere, new and novel type, and the surface being uniformly improved in quality, and a process for producing this resin.

These objects are attained by crosslinking the surface of a water-absorbent polymer powder wherein the average particle diameter being in 100 ~ 600 µm , the particle diameter distribution being 0.35 or less of a logarithmic standard deviation value, σ_ζ , or a water-absorbent polymer powder wherein a ratio between average length and average breadth being 1.5~ 20 and showing an angle-lacking, non-sphere shape.

As methods to obtain a water-absorbent polymer powder having the above-described average particle diameter and particle diameter distribution in this invention, although there have been shown, as examples, a method of an aqueous solution polymerization followed by pulverization and classification to fit in a range of the above-described average particle diameter and particle diameter distribution and a method of reverse-phase suspended polymerization under specified conditions, in order to obtain in a good yield a water-absorbent polymer powder having the above-described average particle diameter and particle diameter distribution and a new, novel shape, the most preferable method is to take a system where, when a reverse-phase suspention polymerization is carried out by using a radical polymerization initiator under conditions that a water-soluble ethylenically unsaturated monomer or its aqueous solution is suspended and dispersed in a hydrophobic organic solvent, the viscosity of an aqueous solution of the water-soluble ethylenically unsaturated monomer determined by a Brookfield rotatory viscosinmeter is adjusted in a value of 15 cps or more and a sucrose fatty acid ester and/or polyglycerol fatty acid ester are used as a dispersing agent.

In perfoming the above-described production process, if the viscosity defined as above is adjusted in a range of 15 ~ 5,000 cps, is obtained in good yields a polymer powder having an average diameter of 100 ~ 600 µm and an index (a logarithmic standard deviation) of 0.35 or less which represents particle diameter distribution.

Furthermore, in perfoming the above-described production process, if the viscosity defined as above is adjusted in a range of 5,000 ~ 1,000,000 cps and, as a dispersing agent, a sucrose fatty acid esters is only used, is obtained in good yields a polymer powder wherein the ratio between length and breadth being in a range of 1.5 ~ 20 and the shape being non-sphere without angle.

As examples of a water-soluble ethylenically unsaturated monomer constituting a water-absorbent resin in the present invention, are cited monomers of anionic character such as acrylic acid, methacrylic acid, crotonic acid, maleic acid and its anhydride, fumaric acid, itaconic acid, and 2-(meth)acryloylethanesulfonic acid, and 2-(meth)acryloylpropanesulfonic acid, and 2-(meth)acrylamido-2-methylpropanesulfonic acid, vinylsulfonic acid, styrenesulfonic acid and the like and their salts; monomers containing nonionic hydrophilic substituent such as (meth)acrylamide, N-substituted (meth) acrylamides, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth) acrylate, methoxypolyethylene glycol (meth)acrylate, poly thylen glycol (meth)-acrylate and the like; monomers of cationic character such as N,N′-dimethylaminoethyl (meth)acrylate, N,N′-diethylaminoethyl (meth)acrylate, N,N′-diethylaminopropyl (meth)acrylate, N,N′-dimethylaminopropyl (meth)acrylamide, and th like and their quartary salts. These compounds can b used as alone or mixture

of two or more compounds. Preferable are a kind of compound or a mixture of two or more compounds chosen from the following three groups of compounds: (meth)acrylic acid, 2-(meth)acryloylethanesulfonic acid, 2-(meth)acrylamido-2-methylpropanesulfonic acid, and their salts; and N,N′-dimethylaminoethyl (meth)acrylate and their quartary salts; and methoxypolyethylene glycol (meth)acrylate and (meth)-acrylamide. Although the monomer concentration in an aqueous monomer solution is generally variable in a wide range, the preferred range is from 20 weight % up to saturation.

The water-absorbent polymer powder used for the present invention comprises a s lf-crosslinking typ prepared in absent of a crosslinking agent and a type co-polymerized during polymerization with a small amount of crosslinking agent, which has polymerizable unsaturated groups or reactive functional groups. As examples of the crosslinking agents are cited N,N′-methylene-bis(meth)acrylamide, N-methylol(meth)-acrylamide, ethylene glycol (meth)acrylate, polyethylene glycol (meth)acrylate, propylene glycol (meth)-acrylate, polypropylene glycol (meth)acrylate, glycerol tri(meth)acrylate, glycerol mono(meth)acrylate, poly-functional metal salts of (meth)acrylic acid, trimethylolpropane tri(meth)acrylate, triallylamine, triallyl cyanulate, triallyl isocyanulate, triallyl phosphate, glycidyl (meth)acrylate. As examples of agents having reactive functional groups for example, in a case that a monomer has a carboxyl and/or carboxylate group, polyhydric alcohol derivatives such as ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, glycerol, polyglycerol, propylene glycol, diethanolamine, triethanolamine, polyoxypropylene, oxyethylene-oxypropylene block co-polymer, pentaerythritol, and sorbitol; polyglycidyl derivatives such as ethylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, glycerol poly-glycidyl ether, diglycerol polyglycidyl ether, polyglycerol polyglycidyl ether, sorbitol polyglycidyl ether, pentaerythritol polyglycidyl ether, propylene glycol diglycidyl ether, and polypropylene glycol diglycidyl ether; aziridine derivatives and related compounds such as 2,2-bishydroxymethylbutanol-tris [3-(1-aziridinyl) propionate] , 1; 6-hexamethylene-diethylene urea, and diphenylmethane-bis-4,4′-N,N′-diethylene urea; haloepoxyl compounds such as epichlorohydrin and α-methylchlorohydrin; polyaldehydes such as glutar aldehyde and glyoxal; poly amine derivatives such as ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, and polyethylene hexamine; polyisocyanates such as 2,4-toluylenediisocyanate and hexamethylenediisocyanate; polyvalent metal salts such as aluminium chloride, magnesium chloride, calcium chloride, aluminium sulfate, magnesium sulfate, and calcium sulfate. Subject to consideration upon reactivity, these crosslinking agents can be used as a mixture of more than two, but it is usually preferable to use a crosslinking agent having polymerizable unsaturated groups. An amount of use of these agents is in general about 0.001 ~1.0 mol. for a water-soluble ethylenically unsaturated monomer.

The most preferable way of obtaining the polymer profitable for the present invention is that the viscosity of an aqueous solution of water-soluble ethylenically unsaturated monomer is adjusted at a value of 15 cps or more when determined with a Brookfield rotatory viscometer (25 °C, 0.6 rpm) (this sort of viscosity is hereinafter referred to as, simply, viscosity) and that the reverse-phase suspension polymerization is performed using a sucrose fatty acid ester and/or a polyglycerol fatty acid ester as a dispersing agent. If the viscosity being below 15 cps, the particle obtained is small in average particle diameter and broad in distribution of particle diameter.

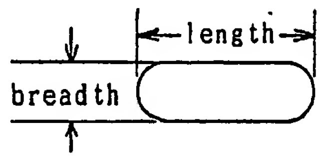
In a method of the present invention wherein a previously-described, specially defined dispersing agent being used, the viscosity of an aqueous solution of water-soluble ethylenically unsaturated monomer being adjusted in a range of 15 ~ 5,000 cps, a water-absorbent polymer of sphere shape being suitable for use in the present invention and having an average particle diameter in a range of 100 ~ 600 μm depending upon viscosity and very narrow distribution of particle diameter can be obtained. Generally under the same condition, the higher the viscosity of an aqueous solution of a monomer becomes, the larger an average particle diameter of the resin obtained becomes, and polymer of various average particle diameters can be obtained with such a simple procedure as an adjustment of viscosity.

Although a preferable average particle diameter of a water-absorbent resin obtained is different depending upon a use, for instance, in a case being used as sanitary materials, the average particle diameter is usually in a range of 100 ~ 600 μm, more preferably about 150 ~ 400 μm. The particle of this kind is obtainable when the viscosity of an aqueous solution being adjusted in a range of 15~ 5,000 cps, more preferably 20 ~ 3,000 cps. In addition, a water-absorbent polymer obtained according to this method shows very narrow distribution of particle diameter.

For instance, when particle distribution is plotted in a logarithmic probability paper, a value of logarithmic standard deviation (σ_ζ), which is an index showing uniformity of a particle, is 0.35 or less, in a more preferable case 0.30 or less, that is narrow particle distribution not yet obtained by any previous method.

In the other side, when the viscosity of an aqueous solution of water-soluble ethylenically unsaturated

monomer is adjusted in a range of 5,000 ~ 1,000,000 cps, although dependent upon stirring condition, the particles obtained shows that the ratio between average length and average breadth for particles as defined as b low-described is in a range of 1.5 ~ 20, and an angle-lacking and non-sphere, so to speak, Vienna sausage-like shape. This polymer has length of 100 ~ 10000 µm, more preferably 1000 ~ 10000 µm and breadth of 10 ~ 2000 µm, more preferably 100 ~ 2000 µm, and a ratio between average length and average breadth being in a range of 1.5~ 20, so that it is easy in handling and treating in point of that it is hard for this polymer to fall off from basis materials, and the range of the combination with different basis materials is spread. The diameters to represent a shape of water-absorbent polymer are defined as follows.



Although being in a range of 5,000 cps or more, when the viscosity is in a range of 5,000 ~ 20,000 cps, a non-sphere polymer and a sphere polymer are obtained as a mixture and, when the viscosity is higher than 20,000 cps, a non-sphere polymer is only obtained. Furthermore, when the viscosity is higher than 1,000,000 cps, there is sometimes accompanied by difficulty when an aqueous solution of monomer being supplied for a reaction vessel.

As the thickener used for adjsting viscosity as described above, are cited hydroxyethylcellulose, hydroxypropylcellulose, methylcellulose, carboxymethylcellulose, polyethylene glycol, polyacrylamide, polyethyleneimine, polyacrylic acid, partially neutralized polyacrylic acid, crosslinked polyacrylic acid, partially neutralized, crosslinked polyacrylic acid, dextrin, and sodium arginate so on. Preferable are hydroxyethylcellulose, polyacrylamide, polyacrylic acid, partially neutralized polyacrylic acid, crosslinked polyacrylic acid, partially neutralized, crosslinked polyacrylic acid. Very specially preferred for a water absorbent-resin having a new shape is hydroxyethylcellulose. For use of a water-soluble, partially neutralized polyacrylic acid, the viscosity of its 5 % aqueous solution is preferred when it is 30 cps or more . For use of a water-insoluble, crosslinked product, is preferred the one whose particle diameter is about 30 µm or less and powder-like.

To thicken an aqueous solution to a designated viscosity by using these thickener, it is preferred that the thickener is generally used in a range of 0.05~ 20 weight % to a monomer, although the percentage is variable with the kind and concentration of a monomer and the kind and molecular weight of a thickener.

In the other side dispersing agents used in this case are sucrose fatty acid esters and/or polyglycerol fatty acid esters. As the former sucrose fatty acid esters, are cited mono-, di-, and triesters derived from sucrose with more than one aliphatic acid chosen from stearic acid, palmitic acid, lauric acid, and oleic acid. As the latter polyglycerol fatty acid esters, are cited mono-, di-, and triesters derived from polyglycerin of condensation degree 10 or less with, at least, one aliphatic acid chosen from stearic acid, palmitic acid, lauric acid, oleic acid, and ricinolic acid. Among all these nonionic surface active agents, most preferable are those indicating HLB of 2~6. The amount of a dispersing agent for use is generally 0.05 ~10 weight % , more preferably 0.5 ~5 weight % against the amount of a water-soluble ethylenically unsaturated monomer. To obtain the water-absorbent polymer having a new non-sphere shape without angle, that is one of the polymers suitable for use in the present invention, the sucrose fatty acid esters can be only used and, if other kinds of dispersing agents are used, this novel type of resin is not obtained.

As an inert hydrophobic organic solvent used for the present invention are cited, for example, aliphatic hydrocarbons such as n-pentane, n-hexane, n-heptane, and n-octane; cycloaliphatic hydrocarbons such as cyclohexane, cyclooctane, methylcyclohexane, decaline, and their derivatives; aromatic hydrocarbons such as benzene, ethylbenzene, toluene, xylene, and their substituted derivatives; and halogenated hydrocarbons such as chlorobenzene, bromobenzene, carbon tetrachloride, and 1,2-dichloroethane. These agents can be used as alone or a mixture of two kinds or more. Specially preferable are n-hexane, n-heptane, cyclohexane, methylcyclohexane, toluene, xylene, and carbon tetrachloride.

The ratio of an organic solvent to a water-soluble ethylenically unsaturated monomer is generally suitable as 1:1 ~ 5:1 from standpoints of steady dispersion and removal of heat generated during polymerization and temperature controll.

As an initiator for radical polymerization in the present invention, any kind of conventional agent can be used without limitation, but particularly, water-soluble ones are preferred. More concretely, for example, persulfates such as potassium persulfate, sodium persulfate, and ammonium persulfate; hydroperoxides

such as hydrogen peroxid , t-butyl hydroperoxide, and cumene hydroperoxide; azo compounds such as 2,2′-azo-bis-2-amidinopropane dihydrochloride etc. are cited. These polymerization initiators can be used as a mixture of more than two agents. Furthermore, a redox type initiator prepared by combination of these polymerization initiators and reducing agents such as sulfite, L-ascorbic acid, and ferric salts may also be used.

In the case where above-described reverse-phase suspension polymerization is performed to obtain a water-absorbent polymer used for the present invention, if it is followed by a drying process, a water-absorbent polymer obtained can be taken out as a bead-like or Vienna sausage-like particle. As this drying process, there are methods wherein water is distilled off as an azeotropic mixture with a hydrophobic organic solvent used in polymerization and wherein filtration of a water-containing gel followed by drying with conventional drying apparatus due to heated wind, reduced pressure, or fluid bed is carried out.

To obtain a polymer powder usable in this invention, not only the above-described reverse-phase suspension polymerization, but also an usable condition is that, when a water-containing gel obtained from an aqueous solution polymerization known in public is dried, pulverized, and classified, the average particle diameter is adjusted in a range of 100 ~ 600 μm and the particle diameter distribution is adjusted at a value of 0.35 or less of σ_ζ .

This invention is attained with uniform quality improvment of a polymer surface by means of surface-crosslinking in a previously known method where the polymer having an average particle diameter in a specially defined range, a narrow distribution of particle diameters, and a sausage shape are obtained according to the above-described method.

A more preferable method is that a polymer powder obtained by drying up to less than 10 weight % of water content is mixed with 0.005 ~ 20 weight % of a crosslinking agent (against the polymer powder) having a reactive group of two or more in its molecule for a functional group in the powder, a reaction is carried out with heating, and said polymer powder is crosslinked in a neighbor of the surface. When the crosslinking agent and the polymer powder being mixed, it is permitted to contain water and a hydrophiric organic solvent.

When this surface-crosslinking treatment being performed, if the treatment condition is chosen from a specially defined ones, the treatment effect becomes superior and an advantage of this process increases. That is, a polymer powder of water content of less than 10 weight % is mixed with a treatment solution composed of 0.005 ~ 20 weight % (more preferable 0.005 ~ 5 weight %) of a crosslinking agent to the polymer powder, 0.1~ 5 weight % of water, and 0.01~ 6 weight % of hydrophilic organic solvent, and thereby, the surface and its neighborhood of polymer power being crosslinked.

When the polymer powder having been obtained from the previously-described procedure, having an average particle diameter in the specially defined range, and showing narrow distribution of particle diameter is mixed with a treatment solution containing a crosslinking agent, any fish eye is not formed, the treatment solution is uniformly dispersed on the surface of the polymer powder, and appropriately permeated in a neighborhood of the polymer powder surface, and as a result, the crosslinking is performed uniformly and with good efficiency. Thus, is obtained a water-absorbent resin wherein water-absorption capacity being high, water-absorption rate and suction force being superior, elution of a water-soluble composition from the resin being small in amount, and as a sanitary material, being very suitable.

In the above described crosslinking process for producing a water-absorbent resin in this invention it is first required to maintain water content of the polymer at a value less than 10 % , more prefarably less than 7 % by the similar process as the above-described one, which was obtained with reverse-phase suspension polymerization. In a case of water content 10 % or more, when a crosslinking agent or the treatment solution containing this is mixed, in addition to that the mixing character is inferior, the crosslinking agent sometimes super-permeates an inside of the resin, so that a water-absorbent resin obtained sometimes has small water-absorption capacity.

As a crossliking agent, which is able to use in this invention, although unlimited as far as it is a compound having two or more of a functional group reactive with functinal groups existing in the polymer, are preferred hydrophilic, more preferred water-soluble compounds. For examples, in a case that the polymer has a carboxyl and/or carboxylate group as a functional group, are cited polyhydric alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, glycerol, polyglycerol, propylene glycol, diethanolamine, triethanolamine, polyoxypropylene, oxyethyleneoxypropylene block copolymer, pentaerythritol, and sorbitol; polyglycidyl compounds such as ethylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, glycerol polyglycidyl ether, diglycerol polyglycidyl ether, polyglycerol polyglycidyl ether, sorbitol polyglycidyl ether, pentaerythritol polyglycidyl ether, propylene glycol diglycidyl ether, and polypropylene glycol diglycidyl ether; polyaziridin derivatives such as 2,2′ -bishydroxymethylbutanol-tris [3-(1-aziridinyl) propionate] , 1,6-hexamethylen di thylenyl ur a, and

diphenylmethane-bis-4,4′-N,N′-diethylenyl urea; haloepoxy compounds such as epichlorohydrine and α-methylchlorohydrine; polyaldehydes such as glutal aldehyde and glyoxal; polyamine derivatives such as ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, and polyethyleneimine; polyisocyanates such as 2,4-toluylenediisocyanate and hexamethylenediisocyanate; polyvalent metal salts such as aluminium chloride, magnesium chloride, calcium chloride, alumunium sulfate, magnesium sulfate, and calcium sulfate. Paticularly preferable are polyhydric alcohols, polyglycidyl compounds, polyamine derivatives, and polyvalent metal salts. The amount of use of these hydrophilic crosslinking agent is 0.005~ 20 weight % against a polymer powder, preferable 0.005 ~ 5 weight %, more preferable 0.01 ~ 1 weight %. In a case that this amount is less than 0.005 weight % , an effect of surface treatment does not appear and also, even if it is used in amount more than 20 weight %, there are some cases where an effect correspond to amount of use of crosslinking agent does not appear and the water absorption capacity remarkably decreases.

In the present invention, if a crosslinking agent is mixed with polymer powder, it is preferable for increase of the treatment effect that the above-described treatment solution containing water and an organic solvent is used. In this case, the amount of water composing a treatment solution is 0.1 ~ 5 weight % against a polymer powder. If this amount is less than 0.1 weight % , a crosslinking agent is not easily permeate a neighborhood of the polymer powder surface, so that a crosslinking surface layer does not properly form. Also, there are some cases where if it exeeds 5 weight % , the agent permeats in exess, so that the water absorption capacity decreases.

As a hydrophilic organic solvent composing of the treatment solution, it is not particularly limited as far as it can dissolve a crosslinking agent and does not affect the performance of a water-absorbent resin. As such, for examples, are cited lower alkohols such as methanol, ethanol, n-propanol, isopropanol, and n-butanol; ketons such as acetone and methylethylketone; ethers such as dioxane and tetrahydrofuran; amides such as N-N′-dimethylformamide; sulfoxides such as dimethylsulfoxide. The amount of use of a hydrophilic organic solvent is 0.1 ~ 6 weight %. In a case that the amount of use of a hydrophlic organic solvent is less than 0.1 weight % , mixing of a polymer with the treatment solution becomes ununiform and also, if the amount exeeds 6 weight % , an effect corresponding to the amount of use can not be obtained and only expense increses, so that it is not industrially favorable. Although dependent upon the kind of hydrophilic organic solvents, it is generally preferable to use 0.3 ~ 4 weight % against a water-absorbent resin.

As a method to mix a treatment solution containing a crosslinking agent with a polymer powder in this invention, it is general to spray or drop and mix the treatment solution for a polymer powder. As a mixer used for mixing, although is preferred the one having a big mixing power to mix uniformly, conventional mixer and kneader can be used. For examples, are cited a cylinder mixer, a double-cone mixer, a V-type mixer, a ribbon mixer, a screw mixer, a fluidized mixer, a rotating-disc type mixer, an air mixer, a double-arm type kneader, an internal mixer, a muller kneader, a roll mixer, and a screw extruder etc. To warm up a composition obtained with mixing a treatment solution containing these crosslinking agents with a polymer powder, a conventional dryer or heating furnace can be used. For examples, are cited a gutter stirring dryer, a rotating dryer, a disc dryer, a kneading dryer, a fluidized dryer, an air dryer, an infrared light dryer, and an dielectrically heating dryer. Temperature for heating treatment is in a range of 40 ~ 250° C, more preferable 80 ~ 200° C.

The water-absorbent resin obtained from the production process in this invention has an average particle diameter in a specially defined range and a narrow distribution of particle diameter and also, has high water absorption capacity and a superior water absorption rate and suction force. In addition, since a water-soluble component existing in an inside of the resin is only eluted in a very small amount from a surface of the resin, the resin is very superior, in particular, in a dispersion character of liquid and in safety when being used as sanitary materials. This kind of water-absorbent resin, as mentioned above, is possible to be produced in the best yield and with high efficiency in the case of that an aqueous solution of water-soluble ethylenically unsaturated monomer, of which viscosity is adjusted at a specially defined value by using a thickener, undergoes a reverse-phase suspension polymerization using a sucrose fatty acid ester and/ or polyglycerol fatty acid ester as a dispersing agent and a polymer obtained is dried and, mixed and warmed with a treatment solution containing a crosslinking agent of a specially defined composition.

Also, such a method involving treatment of a surface part like this case does not require a large amount of organic solvent, so that it is of advantage to economy and industry and a superior water-absorbent resin being of high safety as a sanitary material and various kinds of water-holding materials becam obtainable in a method very useful for producing.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an optical microphotograph to represent a particle structure of th water-absorbent resin of a sphere shape (A16) obtained from exampl 6.

FIG. 2 is an optical microphotograph to represent a particle structure of the water-absorbent resin of a vienna sausage shape (A18) obtained from example 8 .

FIG. 3 is an optical microphotograph to represent a particle structure of the water-absorbent resin (B12) obtained from example for comparison 3.

DETAILED DESCRIPTION OF THE INVENTION

EXAMPLES

Although the present invention is explained in detail with the examples described below, a range of the present invention is not defined within the examples.

The water absorption performance of water-absorbent resin is determined according to the procedure shown below.

(1) Average Particle Diameter and Distribution of Particle Diameter

The resin powder is sifted and classified by using JIS standard sieves(20, 32, 48, 60, 100, 145, 200, and 350 mesh) and then, the remaining percentage (R %) is plotted on a logarithmic probability paper. Average diameter is represented by a particle diameter corresponding to R for 50 %.

The particle distribution is represented by using logarithmic standard deviation, σ_ζ , as an index, which is derived from the following equation:

$$\sigma_\zeta = \frac{1}{2} \ln \frac{x_2}{x_1}$$

(x_1 and x_2 are particle diameters wherein R are equal to 84.1 % and 15.9 % , respectively.)

Here, it is meaned that, as the value of σ_ζ becomes smaller, the particle distribution becomes more uniform.

(2) Water Absorption Capacity

The water-absorbent resin, 0.2 g, is uniformly put into a tea bag-like bag (40 mm × 150 mm) made by a nonwoven fabric, and soaked in a 0.9 weight % aqueous solution of sodium chloride. The teabag-like bag is taken out after 10 minutes and 30 minutes, respectively, and stood for draining for a designated time. Then, the weight is determined and the water absorption capacity is calculated by the following equation. Further, when only the tea bag being soaked, the weight obtained after water absorption is taken as a blank. Water absorption capacity (g / g) = (weight of bag after absorption - blank) / (weight of water-absorption resin)

(3) Water Absorption Rate

To 20 mℓ of synthetic urine containing 1.9 weight % of urea, 0.8 weight % of sodium chloride, 0.1 weight % of calcium chloride, and 0.1 weight % of magnesium sulfate is added 1.0 g of a water-absorbent

resin. The water absorption rate is defined with time passed until the water-absorbent resin absorbing the synthetic urine losts the flowing character of a swelling gel.

(4) Suction force

Water-absorbent resin, 1.0 g, is placed on a material containing synthetic urine, prepared by adding 20 mℓ of synthetic urine on a tissue paper of size 55 mm x 75 mm . After standing for 10 mm , a gel swelled is taken and weighed. The weight is defined as suction force of the resin from the tissue paper. At the same time, the presence of a fish-eye of the added water-absorbent resin was examined.

(5) Amount of Water-Soluble Component Eluted from Resin Surface

A disposable diaper for child composed of a nonwoven fabric, cotton-like pulp, a water-absorbent paper, and a waterproof film (having a weight of 72 g) is cut in half and 2.5 g of a polymer is uniformly scattered between the cotton-pulp and the water-absorbent paper and to this, 120 mℓ of the above-described synthetic urine is added, and the thus-prepared sample is stood for 16 hours at 37° C. After standing for 16 hours, the cotton-like pulp is only taken and a water-soluble component transferred from the pulp is extracted with 1,000 mℓ of pure water. This extract solution is filtered and a polymer component contained in this filtered solution is measured by using an acid-base titration method and thus, a total amount of a water-soluble component eluted is determined against the amount of water-absorbent resin as weight % .

Example 1

In a four-necked separable 2 L flask equipped with a stirrer, a reflux condenser, a thermometer, an inlet tube for nitrogen gas, and a dropping funnel was placed 1,000 mℓ of cyclohexane and dissolved 4.0 g of a sucrose fatty acid ester (DK-ESTER F-50, HLB = 6, a product from DAIICHI KOGYO SEIYAKU Co.,LTD.) and nitrogen gas was introduced into this solution to remove oxygen dissolved. In another flask containing a solution of 84.6 g of sodium acrylate, 21.6 g of acrylic acid, and 0.016 g of N,N′-methylene-bisacrylamide in 197 g of ion-exchanged water was dissolved 0.53 g of hydroxyethylcellulose (HEC-DAISERU EP-850, a product from DAISERU CHEMICAL Co.,LTD.) and was prepared a monomer solution adjusted at a monomer concentration of 35 weight % and viscosity of 40 cps. To this monomer solution was dissolved 0.15 g of potassium persulfate and then, nitrogen gas was introduced to remove oxygen dissolved in this aqueous solution.

Next, to the above separable flask solution was added the aqueous monomer solution in the latter flask and the mixture obtained was dispersed with stirring at 230 rpm. Then, polymerization reaction was initiated by raising bath temperature to 60 °C and completed by maintaining this temperature for 2 hours. After polymerization, the reaction mixture was treated by an azeotropic distillation with cyclohexane to remove water in the water-containing gel , filtered, and dried at 80°C under reduced pressure to obtain a polymer powder of sphere shape (A01). Water content for this polymer powder was 5.6 %.

With 100 weight parts (weight parts are hereinafter referred to as parts) of the polymer powder (A01) was mixed by a paddle type mixer a treatment solution composed of 0.3 parts of diethylene glycol, 4 parts of water, and 0.5 parts of isopropanol. When mixing, any large lump is not formed and all the composition passed through a 20 mesh metal net (mesh of 840 µm) when tried. The composition obtained was treated with heat by a paddle type dryer at 180 °C for 1 hour to obtain a water-absorbent resin (A11). Results obtained from properties measurements for this resin are shown in table 1.

Example 2

Except the use of 2.2 g of hydroxyethylcellulose (SP-600, a product from DAISERU CHEMICAL Co., LTD.), a polymerization reaction was carried out under the same conditions to those for example 1. Viscosity of the monomer aqueous solution was 800 cps and water content of a polymer powder of sphere shape (A02) was 6.8 % . With 100 parts of the polymer powder (A02) was mixed by a paddle typ mixer a treatment solution composed of 0.1 parts of ethylene glycol diglycidyl ether, 3 parts of water, and 6 parts of methanol. When passing is tried, all the composition passed through a 20 mesh metal net. The

composition obtained was treated with heat by a paddle type dryer at 100 °C for 1 hour to obtain a water-absorbent resin (A12). Results obtained from properties measurements for this resin are shown in table 1.

Example 3

Except the use of 3.5 g of hexaglycerol-condensed ricinolate (STEP RP-6, a product from KAO Co., LTD.), a polymerization reaction was carried out in the same way as in example 1 to obtain a polymer powder of sphere shape (A03),which showed water content of 6.3 %. With 100 parts of the polymer powder (A03) was mixed by a V-type mixer a treatment solution composed of 0.08 parts of epichlorohydrin, 2 parts of water, and 4 parts of methanol. When tried, all the composition passed through a 20 mesh metal net and a lump is not observed which may be formed when mixing. The composion obtained was treated with heat by a paddle type dryer at 100 °C for 1 hour to obtain a water-absorbent resin (A13). Results obtained from properties measurements for this resin are shown in table 1.

Example 4

In a four-necked separable 2 L flask equipped with a stirrer, a reflux condenser, a thermometer, an inlet tube for nitrogen gas, and a dropping funnel was placed 1,000 mℓ of cyclohexane and dissolved 4.0 g of a sucrose fatty acid ester (DK-ESTER F-20, a product from DAIICHI KOGYO SEIYAKU Co., LTD.), and nitrogen gas was introduced into this solution to expel oxygen dissolved. In another flask 65.8 g of sodium acrylate, 21.6 g of acrylic acid, 0.076 g of polyethylene glycol diacylate (n = 14), and 15 g of sodium polyacrylate (AQUALIC OM-100, a product from NIPPON SHOKUBAI KAGAKU KOGYO Co., LTD., viscosity of 150 cps at 25 °C for a 5 % aqueous solution) was dissolved in 250 g of ion-exchanged water to prepare an aqueous monomer solution of viscosity of 20 cps.

Next, into this solution, 0.12 g of sodium persulfate was dissolved and a reaction procedure was carried out in the same way as that for example 1 to obtain a polymer powder of sphere shape (A04), which showed water content of 4.8 %.

With 100 parts of the polymer powder (A04) was mixed by a paddle type mixer a treatment solution composed of 1 part of glycerol, 5 parts of water, and 1 part of isopropanol. All the composition passed through a 20 mesh metal net and any lump is not formed at the mixing. Then, the composition obtained was treated with heat by a paddle type dryer at 180 °C for 1.5 hours to obtain a water-absorbent resin (A14). Results obtained from properties measurements for this resin are shown in table 1.

Example 5

Except the use of sodium polyacrylate (AQUALIC FH, 2 × 10^4 cps at 25 °C for viscosity of 1 % aqueous solution, a product from NIPPON SHOKUBAI KAGAKU KOGYO Co., LTD.) as a thickener, a reaction procedure was carried out in the same way as that for example 4 to obtain a polymer powder of sphere shape (A05), showing water content of 5.8 %. The viscosity of an aqueous monomer solution was 27 cps. With 100 parts of the polymer powder (A05) was mixed by a ribbon type mixer a treatment solution composed of 0.05 parts of glycerol glycidyl ether, 4 parts of water, and 0.8 parts of ethanol. All the composition passed through a 20 mesh metal net and, when mixing, any lump did not form. The composition obtained was treated with heat in a fluidized bed dryer at 100 °C for 1 hour to obtain a water-absorbent resin (A15). Results obtained from properties measurements for this resin are shown in table 1.

Example 6

Except that the amount of hydroxyethylcellulose (HEC-DAISERU EP-850, a product from DAISERU KAGAKU KOGYO Co., LTD.) in example 1 was changed into 1.6 g and the viscosity of aqueous monomer solution was adjusted at 2,000 cps, a polymerization reaction was carried out in the same way as that for example 1 to obtain 0.6 g of a water-absorbent polymer powder of all sphere shape (A06), which showed water content of 6.4 %. In the same way as carried out for example 1, this polym r powder (A06) was treated with a surface crosslinking to obtain a water-absorbent resin (A16). Results obtained from properties measurements for this resin are shown in table 1.

Exampl 7

Except that the amount of hydroxyethylcellulose (HEC-DAISERU SP-600, a product from DAISERU KAGAKU KOGYO Co.,LTD.) was 0.3 g and the viscosity of aqueous monomer solution was adjusted at 17 cps, a polymerization reaction was carried out in the same way as that for example 2 to obtain a water-absorbent polymer powder of sphere shape (A07) which showed water content of 5.9 %. In the same way as carried out for example 1, this polymer powder (A07) was treated with a surface crosslinking to obtain a water-absorbent resin (A17). Results obtained from properties measurements for this resin are shown in table 1.

Example 8

In a four-necked separable 2 L flask equipped with a stirrer, a reflux condenser, a thermometer, an inlet tube for nitrogen gas, and a dropping funnel is placed 1,000 mℓ of cyclohexane and dissolved 4.0 g of a sucrose fatty acid ester (DK-ESTER F-50, a product from DAIICHI KOGYO SEIYAKU Co., LTD., HLP = 6) and nitrogen gas was introduced into this solution to remove oxygen dissolved. In another flask containing a solution of 84.6 g of sodium acrylate, 21.6 g of acrylic acid, and 0.016 g of N,N′-methylene-bisacrylamide in 197 g of ion-exchanged water was dissolved 3.2 g of hydroxyethylcellulose (HEC-DAISERU EP-850, a product from DAISERU CHEMICAL Co., LTD.) and was prepared an aqueous monomer solution adjusted at a monomer concentration of 35 weight % and viscosity of 35,000 cps. To this aqueous monomer solution was dissolved 0.15 g of potassium persulfate and then, nitrogen gas was introduced to remove oxygen dissolving in this aqueous solution.

Next, to the above separable flask solution was added the aqueous monomer solution in the latter flask and the mixture obtained was dispersed with stirring at 230 rpm. Then, polymerization reaction was initiated by raising bath temperature to 60 °C and completed by maintaining this temperature for 2 hours. After polymerization completed, the reaction mixture was treated by an azeotropic distillation with cyclohexane to remove water in the water-containing gel, filtered, and dried at 80 °C under reduced pressure to obtain a polymer powder (A08), which had average length of 3,000 µm and average breadth of 550 µm and showed somewhat long and narrow shape of Vienna sausage type. Besides, any sphere particle did not exist.

This polymer powder (A08) was treated with surface crosslinking in the same way as that for example 1 to obtain a water-absorbent resin (A18). Results obtained from properties measurements for this resin are shown in table 1.

Example 9

Except that the amount of a thickener, hydroxyethylcellulose (EP-850, a product of DAISERU KAGAKU KOGYO Co., LTD.) was changed into 5.3 g, a polymerization reaction was carried out in the same way as that for example 8. Viscosity of the aqueous monomer solution was 240,000 cps. After the polymerization completed, treatment with an azeotropic dehydration followed by filtration and drying under reduced pressure gave a polymer powder (A09) having average length of 3500 µm and average breadth of 600 µm and showing a long and narrow shape of Vienna sausage type. Any sphere particle did not exist. This polymer powder (A09) was treated with surface crosslinking in the same way as that for example 2 to obtain a water-absorbent resin (A19). Results obtained from properties measurements for this resin are shown in table 1.

Example 10

Into 329 g of ion-exchanged water was dissolved 141 g of sodium acrylate, 36.1 g of acrylic acid, and 0.118 g of N,N′-methylen-bisacrylamide and, a static aqueous solution polymerization was carried out at 55 ~ 80 °C under a nitrogen atmosphere by using 0.68 g of ammonium persulfate and 0.025 g of sodium hydrogensulfite to obtain a gel-like water-containing polymer, which was dried at 180 °C with a heated wind dryer, pulverized with a hammer-type pulverizer, and sieved with a 28 and a 60 mesh metal nets. The portion, which passed the 28 mesh net but not the 60 mesh net, was taken as a pulverized polymer powder (A010). Treatment of this polymer powder (A010) by surface crosslinking performed in the same way as

that for examle 1 gave a water-absorbent resin (A110). Results obtained from properties measurements for this resin are shown in table 1.

Exampl for Comparison 1

Properties of the polymer powder (A01) obtained from example 1 were measured and summarized in table 1.

Example for Comparison 2

Except that 3.5 g of sorbitane monostearate (REODOL SP-S10, a product from KAO Co., LTD.) was used as a dispersing agent instead of a sucrose fatty acid ester, a polymerization procedure was carried out in the same way as for example 1 to obtain a polymer powder for comparison (B01), which had water content of 6.2 %. The polymer powder for comparison (B01) obtained was mixed with a liquid composition, which is the same as used for example 1, by a paddle type mixer. When mixing, were formed lumps in 8.6 %, which did not pass through a 20 mesh metal net. The compopsition obtained was treated with heat at 180 °C for 1 hour by using a paddle dryer to obtain a water-absorbent resin for comparison (B11). Results obtained from properties measurements for this resin are shown in table 1.

Example for comparison 3

Except no addition of hydroxyethylcellulose to a aqueous monomer solution, the same procedure as for example 1 was carried out to obtain a polymer powder (B02), which showed water content of 4.7 %. At this time, viscosity of a aqueous monomer solution was 7 cps.

The polymer powder for comparison (B02) was mixed by a paddle type mixer with a liquid compposition same as used in example 2. When mixing, were formed lumps in 8.2 % which did not pass through a 20 mesh metal net. The composition obtained was treated with heat by a fluidized bed dryer at 100 °C for 1 hour to obtain a water-absorbent resin for comparison (B12). Results obtained from properties measurements for this resin are shown in table 1.

Example for Comparison 4

Except that 4.0 g of tetraglycerol monostearate (POEMU J-4010, a product from RIKEN VITAMIN Co., LTD.) was used as a dispersing agent instead of a sucrose fatty acid ester used in example 1 and hydroxyethylcellulose was not added to the aqueous monomer solution, a procedure same as for example 1 was carried out to obtain a polymer powder (B03), which showed water content of 5.9 %.

The polymer powder for comparison (B03) was mixed with a liquid composition, which is the same as used for example 1, by a paddle type mixer. When mixing, were formed lumps in 7.6 % which did not pass through a 20 mesh metal net. The composition was treated with heat by a paddle dryer at 180 °C for 1 hour to obtain a water-absorbent resin for comparison (B13). Results obtained from properties measurements for this resin are shown in table 1.

Example for Comparison 5

Properties measured for the polymer powder (A08) in example 8 are shown in table 1.

Example for Comparison 6

In example 10, taking only a part passed through a 28 meth metal net, a polymer powder for comparison (B04) was obtained. Treatment of this polymer powder for comparison (B04) with surface-crosslinkage gave a water-absorbent resin for comparison (B14). Results obtained from properties measurements for this resin are shown in table 1.

Table 1

	Water-absorbent resin obtained	Average particle diameter (μm)	Particle diameter distribution σ_ζ	Amount of lump (%)	Water absorption capacity (g/g)		Water absorption rate (sec.)	Suction force (g)	Formation of fish-eye *	Water-soluble component eluted (%)
					10 min.	30 min.				
Example 1	Water-absorbent resin (A11)	400	0.16	0	59	65	21	18.0	◎	0.15
Example 2	Water-absorbent resin (A12)	500	0.11	0	54	60	33	17.9	◎	0.08
Example 3	Water-absorbent resin (A13)	300	0.15	0	57	63	28	18.8	◎	0.12
Example 4	Water-absorbent resin (A14)	350	0.18	0	60	67	22	18.7	◎	0.07
Example 5	Water-absorbent resin (A15)	350	0.17	0	59	65	19	18.2	◎	0.05
Example 6	Water-absorbent resin (A16)	550	0.19	0	47	64	42	17.6	◎	0.09
Example 7	Water-absorbent resin (A17)	150	0.24	0	52	60	18	18.2	◎	0.13
Example 8	Water-absorbent resin (A18)	sausage-like shape		0	36	51	52	16.2	◎	1.21
Example 9	Water-absorbent resin (A19)	sausage-like shape		0	38	54	49	16.3	◎	0.99
Example 10	Water-absorbent resin (A110)	280	0.16	0	43	62	38	17.8	◎	1.82
Example for comparison 1	Polymer powder (A01)	400	0.16	—	44	62	65	13.2	○	4.2
Example for comparison 2	Water-absorbent resin for comparison (B11)	80	0.43	8.6	45	56	49	15.2	△	3.5
Example for comparison 3	Water-absorbent resin for comparison (B12)	100	0.41	8.2	41	53	45	15.1	△	3.1
Example for comparison 4	Water-absorbent resin for comparison (B13)	150	0.40	7.6	43	55	47	14.8	△	3.3
Example for comparison 5	Water-absorbent resin for comparison (A08)	sausage-like shape		—	28	50	97	11.3	○	4.9
Example for comparison 6	Water-absorbent resin for comparison (B14)	230	0.58	3.5	38	59	47	15.0	△	5.1

(Note) * ◎: No formation of fish-eye at all. ○: Nearly no formation of fish-eye.
△: Some formation of fish-eye.

Claims

1. Water-absorbent resins having average particle diameter of 100 ~ 600 μm, showing particle diameter distribution of 0.35 or less in a value of logarithmic standard deviation, σ_ζ , and being treated with crosslinking on particle surface.

2. Water-absorbent resins of non-sphere, angle-lacking shape wherein a ratio between length and breadth being in a range of 1.5~ 20, and whose particle surface being treated with crosslinking.

3. Water-absorbent resins as claimed in claim 2, wherein the length of particles being in a range of 100 ~ 10,000 μm and the breadth of particles being in a range of 10 ~ 2,000 μm.

4. A process for producing water-absorbent resins wherein the surface of a polymer powder having an average particle diameter of 100 ~ 600 μm and a particle diameter distribution of 0.35 or less in a value of a logarithmic standard deviation, σ_ζ , being treated with crossliking.

5. A process for producing water-absorbent resins wherein the surface of a polymer powder having a ratio of 1.5 ~ 20 between an average particle length and an average particle breadth and showing an angle-lacking, non-sphere shape.

6. A process for producing water-absorbent resins as claimed in claims 4 or 5, wherein the water content of a polymer powder is less than 10 weight % .

7. A process for producing water-absorbent resins as claimed in claims 4, 5, or 6, wherein an aqueous solution of water-soluble ethylenically unsaturated monomer having a viscosity of 15 cps or more, determined by a Brookfield rotational viscometer (25 °C, 0.6 rpm), with using a sucrose fatty acid ester and/or a polyglycerol fatty acid ester as a dispersing agent, being dispersed and suspended in a polymerization-inert hydrophobic organic solvent and polymerized by an initiator for radical polymerization to obtain a polymer powder.

8. A process for producing water-absorbent resins as claimed in claim 7, wherein viscosity of an aqueous solution of water-soluble ethylenically unsaturated monomer being adjusted in a range of 15 ~ 5,000 cps.

9. A process for producing water-absorbent resins as claimed in claim 7, wherein viscosity of an aqueous solution of water-soluble ethylenically unsaturated monomer being adjusted in a range of 5,000 ~ 1,000,000 cps and a sucrose fatty acid ester being only used.

10. A process for producing water-absorbent resins as claimed in claims 4, 5, 6, 7, 8 or 9, wherein, when being treated with crosslinking, an agent having in the molecule two or more of a group reactive for a functional group of the polymer powder is used.

11. A process for producing water-absorbent resins as claimed in claim 10, wherein the crosslinking agent is used in form of a treatment solution prepared by mixing this agent with water and a hydrophilic organic solvent.

12. A process for producing water-absorbent resins as claimed in claim 11, wherein the composition proportions of a crosslinking agent, water, and a hydrophilic organic solvent are adjusted as, against the polymer powder, 0.005 ~ 20 weight %, 0.1 ~ 5 weight %, and 0.01 ~ 6 weight % , respectively.

13. A process for producing water-absorbent resins as claimed in claim 11 or 12, wherein a polymer powder is mixed with a treatment solution, then warmed at 40 ~ 250 °C and the surface of above-described polymer powder is treated with crossliking.

Fig.1

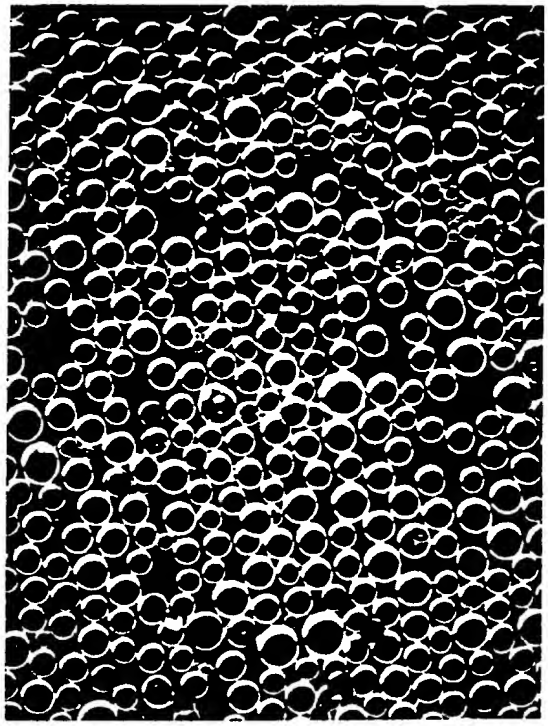
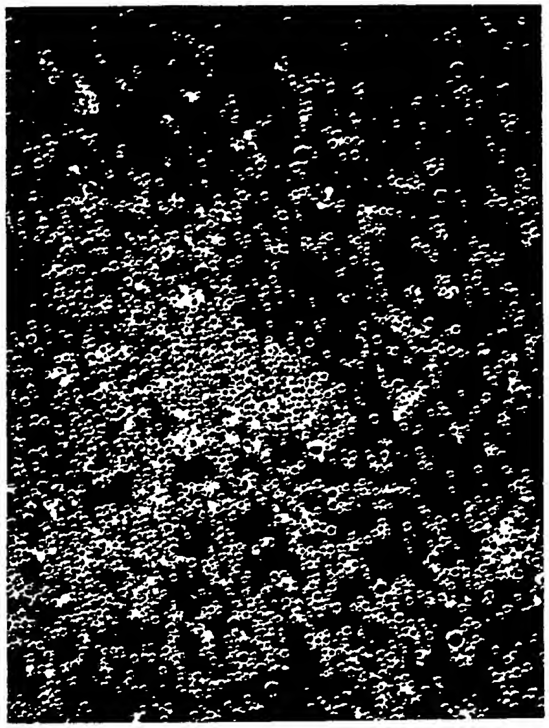


Fig.2

Fig. 3



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(54) Water-absorbent resin and production process.

(57) This invention relates to a water-absorbent resin of new, novel type obtained from polymerization of a water-soluble ethylenically unsaturated monomer followed by surface treatment and, in addition, a process for producing this resin.

The water-absorbent resin in this invention has average particle diameter in a specially defined range and a narrow range of particle distribution. And furthermore, since the particle surface is treated with crosslinking, a balance is very good among water absorption properties, for example, between water absorption capacity and water absorption rate, and between gel strength and suction force. This water-absorbent resin is takable a angle-lacking, non-sph re shape and in a case of this type of shape, it is superior in such handling properties as falling off from an basis material being hard.

Since the production process in the present invention comprises crosslinking treatment for the particle surface of a specially defined water-absorption polymer, the crosslinking is performed with good efficiency and, a water-absorption resin being superior in a balance among water absorption properties is obtainable with an economic advantage. This specially defined water-absorption polymer particle is obtained by polymerizing a water-soluble ethylenically unsaturated monomer in a process of reverse-phase suspension polymerization. In the production process of this invention, since the aqueous monomer solution is chosen from those in a specially defined viscosity rang and then, disp rsed and suspended by using a sp cially defined dispersing agent, a specially defined water-absorb nt resin is easily obtainable wh rein, not only th average particle diameter is controlled by adjusting the viscosity of an aqueous monomer solution, but also th

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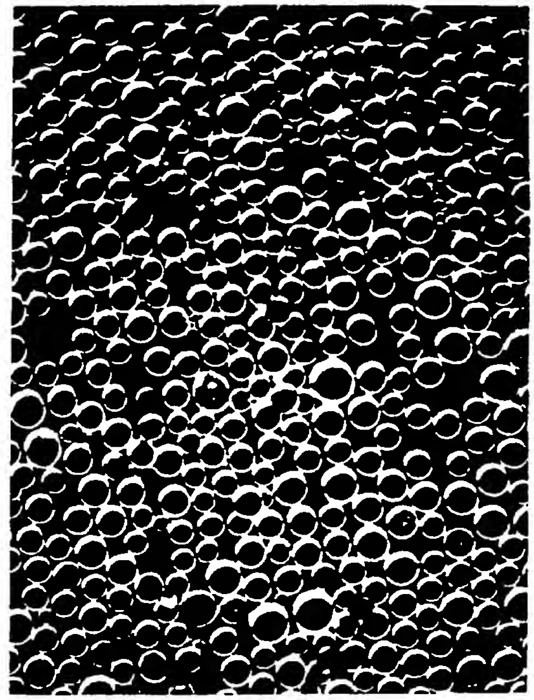
particle diameter distribution resulted is narrow.

In this production process, th particle shape can be changed by changing up and down the viscocity of an aqueous solution of monomer in the above-described sp cially defined range.

The water-absorbent resin in this invention, because it has the above-described properties, is preferably used for sanitary materials and the like.

Fig.1



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EUROPEAN SEARCH REPORT

Application Numb r

EP 89 30 6461

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 176 664 (SEITETSU KAGAKU CO.) * Claims; page 12, line 5 - page 13, line 4 * - - -	1	C 08 F 2/32 A 61 L 15/00
A		7,9,10	
A	GB-A-2 126 591 (KAO CORP.) * The whole document * - - -	7,10-13	
X	EP-A-0 234 202 (SEITETSU KAGAKU CO.) * Claims; page 12, line 1 - page 14, line 20 * - - -	1	
A	- - - - -	7,10	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
C 08 F A 61 L

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	31 January 91	ANDRIOLLO G.R.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
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(54) Water-absorbent resin and production process

Wasserabsorbierendes Harz und seine Herstellung

Résine absorbant de l'eau et son procédé de préparation

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BACKGROUND OF THE INVENTION

This invention relat s to a water-absorbent resin and a process for producing this resin. In detail, it relates to a water-absorbent resin having average particle diameter in a specially defined range, narrow range of particle distribution, and a surface of uniformly improved quality and, in particular, being superior in water absorption capacity, water absorption rate, suction force, and gel strength, showing that water absorption properties are in good balance, showing that the amount of elution of water-soluble resin (hereinafter referred to as water-soluble component) is only small, and being very suitable as sanitary materials, and also, a process for producing the water-absorbent resin.

Hitherto, an attempt has been carried out to use a water-absorbent resin as an absorbent sanitary material for absorbing body fluids such as a sanitary cotton, a disposable diaper, and the like. There have been known, as water-absorbent resins for this purpose, a hydrolyzed starch-acrylonitrile graft polymer (Japanese Official Patent Gazette, shouwa 49-43395), a neutralized starchacrylic acid graft polymer (Japanese Official Patent Provisional Publication, shouwa 51-125468), a saponified vinyl acetate-acrylic acid ester copolymer (Japanese Official Patent Provisional Publication, shouwa 52-14689), a hydrolyzed acrylonitrile or acrylamide copolymer (Japanese Official Patent Gazette, Shouwa 53-15959), and crosslinked products of these polymers, a crosslinked product of a partially neutralized polyacrylic acid (Japanese Official Patent Provisional Publication, Shouwa 55-84304).

Incidentally, as properties to be wanted for water-absorbent resins, are cited high water absorption capacity, a water absorption rate, and high gel strength of water-contained swelling gel when the resins are coming in contact with aqueous liquid, and superior suction force to suck up water from a basic material containing aqueous liquid. These properties hitherto have been in a poor balance. That is, these properties are not in directly proportional relation, in particular, water absorption capacity and water absorption rate or gel strength and suction force are in reversely proportional relation, so that there has been found a trend that, as the water absorption capacity increases, other properties decrease. When some resins of a high water-absorbent capacity come in contact with aqueous liquid, aqueous liquid does not spread over the whole part of a water-absorbent resin and the resins form lumps, that is, what we call fish-eyes, so that an an extreme lowering of a water absorption rate is observed. Also, in a case of that these water-absorbent resins are used for an absorption body of sanitary materials, the above-described water-soluble component being contained in the water-absorbent resins affects on the absorption capacity of an absorption body, liquid-spreading in a absorption body, and so on.

Especially, as the water-absorption capacity for a water-absorption resin increases, elution of a water-soluble component increases in amount, so that there has been found a problem that the resin can not properly used as sanitary materials.

As methods to improve the above-described properties with maintaining their good balance, there have been proposed methods to improve such properties as a water absorption rate etc. by crosslinking the surface of an obtained water-absorbent resin, without giving damage for water absorption capacity which the water-absorbent resin itself has. They are a method wherein a water-absorbent resin being dispersed in a hydrophilic organic solvent or a hydrophobic organic solvent in presence of water and undergoing to react in addition of a crosslinking agent (or its aqueous solution) (Japanese Official Patent Gazette, shouwa 61-48521 and 60-18690) and a method wherein a water-absorbent resin powder was mixed with a crosslinking agent or a liquid composition containing a crosslinking agent to treat with heat (Japanese Official Patent Provisional Publication, shouwa 58-180233, 59-189103, and 61-16903).

In these cases, of importance are uniform dispersion of a crosslinking agent over the surface of a water-absorbent resin and proper permeation into a neighborhood of the surface and, in addition, it is liked that the process is of advantage to industry. However, hitherto known methods have had problems in these points. That is, in the method wherein a water-absorbent resin being dispersed in a solvent and undergoing a crosslinking reaction, a large amount of solvent is required and so, its recovery process is of disadvantage to industry. Especially, in a case being carried out in a hydrophobic organic solvent, distribution of a crosslinking agent on the surface of a water-absorbent resin is apt to become ununiform, so that the crosslinking of surface becomes ununiform. On the other hand, the method wherein a water-absorbent resin is mixed with a liquid component containing a crosslinking agent and treated with heat, is of great advantage to industry, and however, in a case of that particle diameter of a water-absorbent resin is small or distribution of particle diameter is broad, there was found a case that, though being affected on a treatment solution mixing with the water-absorbent resin powder, the powder meets together making a large lump (a fish-eye) and so, it is rather hard to crosslink uniformly the surface. Futhermore, though by doing these treatments such properties as water absorption rate and suction force are somewhat improved, but the improvement is still insufficient and, in particular, elution of a water-soluble component could not be prevented. Thus, has not yet found a method sufficiently satisfied in point of that various kinds of properties of a water-absorbent resin are improved maintaining good balance of properties.

BRIEF SUMMARY OF THE INVENTION

According to the present invention, there is provided a water-absorbent resin comprising anionic group-containing polymer particles having an average particle diameter of 100-600 μm, showing particle diameter distribution of 0.35 or less in a value of logarithmic standard deviation, $\sigma\zeta$, and being further treated with a cross-linking agent to provide crosslinking on the particle surface.

The present invention also provides a method for producing a water-absorbent resin, said method comprising cross-linking the surface and neighbourhood of said surface of polymer powder particles having an average particle diameter in the range of 100-600 μm and a particle diameter distribution of 0.35 or less by logarithmic standard deviation ($\sigma\zeta$), the polymer being obtained by polymerisation of an aqueous solution of an anionic water-soluble ethylenically unsaturated monomer wherein the crosslinking is obtained by treating the polymer with 0.005 to 20 weight %, based on the polymer powder, of a crosslinking agent.

Suitably, the water content of the polymer powder is less than 10 weight %.

Preferably also said crosslinking agent has in the molecule two or more groups reactive to a functional group of the polymer powder.

Preferably the polymer powder is mixed with the treatment solution, then warmed at 40 ~ 250 °C.

More preferably said polymer powder is manufactured by a process where an aqueous solution of an anionic water-soluble ethylenically unsaturated monomer having a viscosity of 15 ~ 5,000 cps, determined by a Brookfield rotational viscometer (25 °C, 0.6 rpm), and being at least 20 weight % soluble in water, using a sucrose fatty acid ester and/or a polyglycerol fatty acid ester as a dispersing agent is dispersed and suspended in a polymerisation-inert hydrophobic organic solvent and is polymerized by a radical initiator for radical polymerization to obtain a polymer powder.

Preferably said polymer powder is manufactured by a process where an aqueous solution of anionic water-soluble ethylenically unsaturated monomer is polymerized to obtain a gel-like water-containing polymer, said gel-like water-containing polymer is dried, and the dried polymer is pulverized and classified to obtain a polymer powder.

Preferably the agent responsible for crosslinking the surface and neighbourhood of said surface is used in the form of a treatment solution with water and a hydrophilic organic solvent.

Preferably the treatment solution comprises 0.005%-20% crosslinking agent, 0.1-5% water and 0.01-6% hydrophilic organic solvent by weight relative to the polymer powder.

As methods to obtain a water-absorbent polymer powder having the above-described average particle diameter and particle diameter distribution in this invention, although there have been shown, as examples, a method of an aqueous solution polymerization followed by pulverization and classification to fit in a range of the above-described average particle diameter and particle diameter distribution and a method of reverse-phase suspended polymerization under specified conditions, in order to obtain in a good yield a water-absorbent polymer powder having the above-described average particle diameter and particle diameter distribution and a new, novel shape, the most preferable method is to take a system where, when a reverse-phase suspension polymerization is carried out by using a radical polymerization initiator under conditions that a water-soluble ethylenically unsaturated monomer or its aqueous solution is suspended and dispersed in a hydrophobic organic solvent, the viscosity of an aqueous solution of the water-soluble ethylenically unsaturated monomer determined by a Brookfield rotary viscometer is adjusted in a value of 15cps or more and a sucrose fatty acid ester and/or polyglycerol fatty acid ester are used as a dispersing agent.

In performing the above-described production process, if the viscosity defined as above is adjusted in a range of 15 - 5,000 cps, is obtained in good yields a polymer powder having an average diameter of 100 - 600 μm and an index (a logarithmic standard deviation) of 0.35 or less which represents particle diameter distribution.

Furthermore, in performing the above-described production process, if the viscosity defined as above is adjusted in a range of 5,000 - 1,000,000 cps and, as a dispersing agent, a sucrose fatty acid ester is only used, there is obtained in good yields a polymer powder wherein the ratio between length and breadth being in a range of 1.5 - 20 and the shape being non-sphere without angle.

As examples of a water-soluble ethylenically unsaturated monomer constituting a water-absorbent resin in the present invention, are cited monomers of anionic character such as acrylic acid, methacrylic acid, crotonic acid, maleic acid and its anhydride, fumaric acid, itaconic acid and 2-(meth)acryloylethanesulfonic acid, and 2-(meth)acryloylpropanesulfonic acid, and 2-(meth)acrylamido-2-methylpropanesulfonic acid, vinylsulfonic acid, styrenesulfonic acid and their salts; monomers containing nonionic hydrophilic substituent such as (meth)acrylamide, N-substituted (meth) acrylamides, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth) acrylate, methoxypolyethylene glycol (meth)acrylate and polyethylene glycol (meth)acrylate; monomers of cationic character such as N,N'-dimethylaminoethyl (meth)acrylate, N,N'-diethylaminoethyl (meth)acrylate, N,N'-diethylaminopropyl (meth)acrylate and N,N'-dimethylaminopropyl (meth)acrylamide and their quartary salts. These compounds can be used as alone or mixture of two or more compounds. Preferable are a kind of compound or a mixture of two or more compounds chosen from the following three groups of compounds: (meth)acrylic acid, 2-(meth 2-(meth)acryloylethanesulfonic acid, 2-(meth) acrylamido-2-methylpropanesulfonic acid, and their salts; and N,N'-dimethylaminoethyl (meth)acrylate and their quartary salts; and meth-

oxypolyethylene glycol (meth)acrylate and (meth)acrylamide. Although the monomer concentration in an aqueous monomer solution is generally variable in a wide range, the preferred range is from 20 weight % up to saturation.

The water-absorbent polymer powder used for the present invention comprises a self-crosslinking type pr pared in the absence of a crosslinking agent and a type co-polymerized during polymerization with a small amount of crosslinking agent, which has polymerizable unsaturated groups or reactive functional groups. As examples of the crosslinking agents are cited N,N'-methylene-bis(meth)acrylamide, N-methylol(meth)acrylamide, ethylene glycol (meth)acrylate, polyethylene glycol (meth)acrylate, propylene glycol (meth)acrylate, polypropylene glycol (meth)acrylate, glycerol tri (meth)acrylate, glycerol mono(meth)acrylate, polyfunctional metal salts of (meth) acrylic acid, trimethylolpropane tri (meth)acrylate, triallylamine, triallyl cyanurate, triallyl isocyanurate, triallyl phosphate, glycidyl (meth)acrylate. As examples of agents having reactive functional groups for example, in a case that a monomer has a carboxyl and/or carboxylate group, polyhydric alcohol derivatives such as ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, glycerol, polyglycerol, propylene glycol, diethanolamine, triethanolamine, polyoxypropylene, oxyethylene-oxypropylene block co-polymer, pentaerythritol, and sorbitol; polyglycidyl derivatives such as ethylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, glycerol polyglycidyl ether, diglycerol polyglycidyl ether, polyglycerol polyglycidyl ether, sorbitol polyglycidyl ether, pentaerythritol polyglycidyl ether, propylene glycol diglycidyl ether, and polypropylene glycol diglycidyl ether; aziridine derivatives and related compounds such as 2,2-bishydroxymethylbutanol-tris [3-(1-aziridinyl) propionate] , 1; 6-hexamethylene-diethylene urea, and diphenylmethane-bis-4,4'-N,N'-diethylene urea; haloepoxyl compounds such as epichlorohydrin and α-methylchlorohydrin; polyaldehydes such as glutar aldehyde and glyoxal; poly amine derivatives such as ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, and polyethylene hexamine; polyisocyanates such as 2,4-toluylenediisocyanate and hexamethylenediisocyanate; polyvalent metal salts such as aluminium chloride, magnesium chloride, calcium chloride, aluminium sulfate, magnesium sulfate, and calcium sulfate. Subject to consideration upon reactivity, these crosslinking agents can be used as a mixture of more than two, but it is usually preferable to use a crosslinking agent having polymerizable unsaturated groups. An amount of use of these agents is in general about 0.001 ~1.0 mol. for a water-soluble ethylenically unsaturated monomer.

The most preferable way of obtaining the polymer profitable for the present invention is that the viscosity of an aqueous solution of water-soluble ethylenically unsaturated monomer is adjusted at a value of 15 cps or more when determined with a Brookfield rotatory viscometer (25 °C, 0.6 rpm) (this sort of viscosity is hereinafter referred to as, simply, viscosity) and that the reverse-phase suspension polymerization is performed using a sucrose fatty acid ester and/or a polyglycerol fatty acid ester as a dispersing agent. If the viscosity being below 15 cps, the particle obtained is small in average particle diameter and broad in distribution of particle diameter.

In a method of the present invention wherein a previously-described, specially defined dispersing agent being used, the viscosity of an aqueous solution of water-soluble ethylenically unsaturated monomer being adjusted in a range of 15 ~ 5,000 cps, a water-absorbent polymer of sphere shape being suitable for use in the present invention and having an average particle diameter in a range of 100 ~ 600 µm depending upon viscosity and very narrow distribution of particle diameter can be obtained. Generally under the same condition, the higher the viscosity of an aqueous solution of a monomer becomes, the larger an average particle diameter of the resin obtained becomes, and polymer of various average particle diameters can be obtained with such a simple procedure as an adjustment of viscosity.

Although a preferable average particle diameter of a water-absorbent resin obtained is different depending upon a use, for instance, in a case being used as sanitary materials, the average particle diameter is usually in a range of 100 ~ 600 µm, more preferably about 150 ~ 400 µm. The particle of this kind is obtainable when the viscosity of an aqueous solution being adjusted in a range of 15 ~ 5,000 cps, more preferably 20 ~ 3,000 cps. In addition, a water-absorbent polymer obtained according to this method shows very narrow distribution of particle diameter.

For instance, when particle distribution is plotted in a logarithmic probability paper, a value of logarithmic standard deviation (σ_ζ), which is an index showing uniformity of a particle, 0.35 or less, in a more preferable case 0.30 or less, that is narrow particle distribution not yet obtained by any previous method.

As the thickener used for adjsting viscosity as described above, are cited hydroxyethylcellulose, hydroxypropylcellulose, methylcellulose, carboxymethylcellulose, polyethylene glycol, polyacrylamide, polyethyleneimine, polyacrylic acid, partially neutralized polyacrylic acid, crosslinked polyacrylic acid, partially neutralized, crosslinked polyacrylic acid, dextrin, and sodium arginate. Preferable are hydroxyethylcellulose, polyacrylamide, polyacrylic acid, partially neutralized polyacrylic acid, crosslinked polyacrylic acid, partially neutralized, crosslinked polyacrylic acid. Very specially preferred for a water absorbent-resin having a new shape is hydroxyethylcellulose. For use of a water-soluble, partially neutralized polyacrylic acid, the viscosity of its 5 % aqueous solution is preferred when it is 30 cps or more For use of a water-insoluble, crosslinked product, is preferred the one whose particle diameter is about 30 µm or less and powder-like.

To thicken an aqueous solution to a designated viscosity by using these thickener, it is preferred that the thickener is generally used in a range of 0.05~ 20 weight % to a monomer, although the percentage is variable with the kind

and concentration of a monomer and the kind and molecular weight of a thickener.

In the other side dispersing agents used in this case are sucrose fatty acid esters and/or polyglycerol fatty acid esters. As the former sucrose fatty acid esters, are cited mono-, di-, and triesters derived from sucrose with mor than one aliphatic acid chosen from stearic acid, palmitic acid, lauric acid, and oleic acid. As the latter polyglycerol fatty acid esters, are cited mono-, di-, and triesters derived from polyglycerin of condensation degre 10 or less with, at least, one aliphatic acid chosen from stearic acid, palmitic acid, lauric acid, oleic acid, and ricinolic acid. Among all these nonionic surface active agents, most preferable are those indicating HLB of 2~6. The amount of a dispersing agent for use is generally 0.05 ~10 weight %, more preferably 0.5 ~5 weight % against the amount of a water-soluble ethylenically unsaturated monomer. To obtain the water-absorbent polymer having a new non-sphere shape without angle, that is one of the polymers suitable for use in the present invention, the sucrose fatty acid esters can be only used and, if other kinds of dispersing agents are used, this novel type of resin is not obtained.

As an inert hydrophobic organic solvent used for the present invention are cited, for example, aliphatic hydrocarbons such as n-pentane, n-hexane, n-heptane, and n-octane; cycloaliphatic hydrocarbons such as cyclohexane, cyclooctane, methylcyclohexane, decaline, and their derivatives; aromatic hydrocarbons such as benzene, ethylbenzene, toluene, xylene, and their substituted derivatives; and halogenated hydrocarbons such as chlorobenzene, bromobenzene, carbon tetrachloride, and 1,2-dichloroethane. These agents can be used as alone or a mixture of two kinds or more. Specially preferable are n-hexane, n-heptane, cyclohexane, methylcyclohexane, toluene, xylene, and carbon tetrachloride.

The ratio of an organic solvent to a water-soluble ethylenically unsaturated monomer is generally suitable as 1:1 ~ 5:1 from standpoints of steady dispersion and removal of heat generated during polymerization and temperature controll.

As an initiator for radical polymerization in the present invention, any kind of conventional agent can be used without limitation, but particularly, water-soluble ones are preferred. More concretely, for example, persulfates such as potassium persulfate, sodium persulfate, and ammonium persulfate; hydroperoxides such as hydrogen peroxide, t-butyl hydroperoxide, and cumene hydroperoxide; azo compounds such as 2,2'-azo-bis-2-amidinopropane dihydrochloride are cited. These polymerization initiators can be used as a mixture of more than two agents. Furthermore, a redox type initiator prepared by combination of these polymerization initiators and reducing agents such as sulfite, L-ascorbic acid, and ferric salts may also be used.

In the case where above-described reverse-phase suspension polymerization is performed to obtain a water-absorbent polymer used for the present invention, if it is followed by a drying process, a water-absorbent polymer obtained can be taken out as a bead-like or Vienna sausage-like particle. As this drying process, there are methods wherein water is distilled off as an azeotropic mixture with a hydrophobic organic solvent used in polymerization and wherein filtration of a water-containing gel followed by drying with conventional drying apparatus due to heated wind, reduced pressure, or fluid bed is carried out.

To obtain a polymer powder usable in this invention, not only the above-described reverse-phase suspension polymerization, but also an usable condition is that, when a water-containing gel obtained from an aqueous solution polymerization known in public is dried, pulverized, and classified, the average particle diameter is adjusted in a range of 100 ~ 600 µm and the particle diameter distribution is adjusted at a value of 0.35 or less of σ_ζ.

This invention is attained with uniform quality improvment of a polymer surface by means of surface-crosslinking in a previously known method where the polymer having an average particle diameter in a specially defined range, a narrow distribution of particle diameters, and a sausage shape are obtained according to the above-described method.

A more preferable method is that a polymer powder obtained by drying up to less than 10 weight % of water content is mixed with 0.005 ~ 20 weight % of a crosslinking agent (against the polymer powder) having a reactive group of two or more in its molecule for a functional group in the powder, a reaction is carried out with heating, and said polymer powder is crosslinked in the neighbourhood of the surface. When the crosslinking agent and the polymer powder being mixed, it is permitted to contain water and a hydrophilic organic solvent.

When this surface-crosslinking treatment being performed, if the treatment condition is chosen from a specially defined ones, the treatment effect becomes superior and an advantage of this process increases. That is, a polymer powder of water content of less than 10 weight % is mixed with a treatment solution composed of 0.005 ~ 20 weight % (more preferable 0.005 5 5 weight %) of a crosslinking agent to the polymer powder, 0,1~ 5 weight % of water, and 0.01~ 6 weight % of hydrophilic organic solvent, and thereby, the surface and its neighbourhood of polymer power being crosslinked.

When the polymer powder having been obtained from the previously-described procedure, having an average particle diameter in the specially defined range, and showing narrow distribution of particle diameter is mixed with a treatment solution containing a crosslinking agent, any fish eye is not formed, the treatment solution is uniformly dispersed on the surface of the polymer powder, and appropriately permeated in the neighbourhood of the polymer powder surface, and as a result, the crosslinking is performed uniformly and with good efficiency. Thus, is obtained a water-absorbent resin wherein water-absorption capacity being high, water-absorption rat and suction force being superior,

elution of a water-soluble composition from the resin being small in amount, and as a sanitary material, being very suitable.

In the above described crosslinking process for producing a water-absorbent resin in this invention it is first required to maintain water content of the polymer at a value less than 10 %, more preferably less than 7 % by the similar process as the above-described one, which was obtained with reverse-phase suspension polymerization. In a case of water content 10 % or more, when a crosslinking agent or the treatment solution containing this is mixed, in addition to that the mixing character is inferior, the crosslinking agent sometimes super-permeates an inside of the resin, so that a water-absorbent resin obtained sometimes has small water-absorption capacity.

As a crossliking agent, which is able to use in this invention, although unlimited as far as it is a compound having two or more of a functional group reactive with functional groups existing in the polymer, are preferred hydrophilic, more preferred water-soluble compounds. For examples, in a case that the polymer has a carboxyl and/or carboxylate group as a functional group, are cited polyhydric alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, glycerol, polyglycerol, propylene glycol, diethanolamine, triethanolamine, polyoxypropylene, oxyethyleneoxypropylene block copolymer, pentaerythritol, and sorbitol; polyglycidyl compounds such as ethylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, glycerol polyglycidyl ether, diglycerol polyglycidyl ether, polyglycerol polyglycidyl ether, sorbitol polyglycidyl ether, pentaerythritol polyglycidyl ether, propylene glycol diglycidyl ether, and polypropylene glycol diglycidyl ether; polyaziridine derivatives such as 2,2'-bishydroxymethylbutanol-tris [3-(1-aziridinyl) propionate], 1,6-hexamethylenediethylenyl urea, and diphenylmethane-bis-4,4'-N,N'-diethylenyl urea; haloepoxy compounds such as epichlorohydrine and α-methylchlorohydrine; polyaldehydes such as glutal aldehyde and glyoxal; polyamine derivatives such as ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, and polyethyleneimine; polyisocyanates such as 2,4-toluylenediisocyanate and hexamethylenediisocyanate; polyvalent metal salts such as aluminium chloride, magnesium chloride, calcium chloride, alumunium sulfate, magnesium sulfate, and calcium sulfate. Particularly preferable are polyhydric alcohols, polyglycidyl compounds, polyamine derivatives, and polyvalent metal salts. The amount of use of these hydrophilic crosslinking agent is 0.005~ 20 weight % against a polymer powder, preferable 0.005 ~ 5 weight %, more preferable 0.01 ~ 1 weight %. In a case that this amount is less than 0.005 weight %, an effect of surface treatment does not appear and also, even if it is used in amount more than 20 weight %, there are some cases where an effect correspond to amount of use of crosslinking agent does not appear and the water absorption capacity remarkably decreases.

In the present invention, if a crosslinking agent is mixed with polymer powder, it is preferable for increase of the treatment effect that the above-described treatment solution containing water and an organic solvent is used. In this case, the amount of water composing a treatment solution is 0.1 ~ 5 weight % against a polymer powder. If this amount is less than 0.1 weight %, a crosslinking agent is not easily permeate a neighborhood of the polymer powder surface, so that a crosslinking surface layer does not properly form. Also, there are some cases where if it exeeds 5 weight %, the agent permeats in excess, so that the water absorption capacity decreases.

As a hydrophilic organic solvent composing of the treatment solution, it is not particularly limited as far as it can dissolve a crosslinking agent and does not affect the performance of a water-absorbent resin. As such, for examples, are cited lower alcohols such as methanol, ethanol, n-propanol, isopropanol, and n-butanol; ketons such as acetone and methylethylketone; ethers such as dioxane and tetrahydrofuran; amides such as N-N'-dimethylformamide; sulfoxides such as dimethylsulfoxide. The amount of use of a hydrophilic organic solvent is 0.1 ~ 6 weight %. In a case that the amount of use of a hydrophlic organic solvent is less than 0.1 weight %, mixing of a polymer with the treatment solution becomes ununiform and also, if the amount exeeds 6 weight %, an effect corresponding to the amount of use can not be obtained and only expense increases, so that it is not industrially favorable. Although dependent upon the kind of hydrophilic organic solvents, it is generally preferable to use 0.3 ~ 4 weight % against a water-absorbent resin.

As a method to mix a treatment solution containing a crosslinking agent with a polymer powder in this invention, it is general to spray or drop and mix the treatment solution for a polymer powder. As a mixer used for mixing, although is preferred the one having a big mixing power to mix uniformly, conventional mixer and kneader can be used. For examples, are cited a cylinder mixer, a double cone mixer, a V-type mixer, a ribbon mixer, a screw mixer, a fluidized mixer, a rotating-disc type mixer, an air mixer, a double-arm type kneader, an internal mixer, a muller kneader, a roll mixer, and a screw extruder. To warm up a composition obtained with mixing a treatment solution containing these crosslinking agents with a polymer powder, a conventional dryer or heating furnace can be used. For examples, are cited a gutter stirring dryer, a rotating dryer, a disc dryer, a kneading dryer, a fluidized dryer, an air dryer, an infrared light dryer, and an dielectrically heating dryer. Temperature for heating treatment is in a range of 40 ~ 250°C, more preferable 80 ~ 200°C.

The water-absorbent resin obtained from the production process in this invention has an average particle diameter in a specially defined range and a narrow distribution of particle diameter and also, has high water absorption capacity and a superior water absorption rate and suction force. In addition, since a water-soluble component existing in an inside of the resin is only eluted in a very small amount from a surface of the resin, the resin is very superior, in particular,

in a dispersion character of liquid and in safety when being used as sanitary materials. This kind of water-absorbent resin, as mentioned above, is possible to be produced in the best yield and with high efficiency in the case of that an aqueous solution of water-soluble ethylenically unsaturated monomer, of which viscosity is adjusted at a specially defined value by using a thickener, undergoes a reverse-phase suspension polymerization using a sucrose fatty acid ester and/ or polyglycerol fatty acid ester as a dispersing agent and a polymer obtained is dried and, mixed and warmed with a treatment solution containing a crosslinking agent of a specially defined composition.

Also, such a method involving treatment of a surface part like this case does not require a large amount of organic solvent, so that it is of advantage to economy and industry and a superior water-absorbent resin being of high safety as a sanitary material and various kinds of water-holding materials became obtainable in a method very useful for producing.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an optical microphotograph to represent a particle structure of the water-absorbent resin of a sphere shape (A16) obtained from example 6.

FIG. 2 is an optical microphotograph to represent a particle structure of the water-absorbent resin (B12) obtained from example for comparison 3.

DETAILED DESCRIPTION OF THE INVENTION

EXAMPLES

The water absorption performance of water-absorbent resin is determined according to the procedure shown below.

(1) Average Particle Diameter and Distribution of Particle Diameter

The resin powder is sifted and classified by using JIS standard sieves(20, 32, 48, 60, 100, 145, 200, and 350 mesh) and then, the remaining percentage (R %) is plotted on a logarithmic probability paper. Average diameter is represented by a particle diameter corresponding to R for 50 %.

The particle distribution is represented by using logarithmic standard deviation, σ_ζ , as an index, which is derived from the following equation:

$$\sigma_\zeta = \frac{1}{2} \ln \frac{x_2}{x_1}$$

(x_1 and x_2 are particle diameters wherein R are equal to 84.1 % and 15.9 % , respectively.)

Here, it is meaned that, as the value of σ_ζ becomes smaller, the particle distribution becomes more uniform.

(2) Water Absorption Capacity

The water-absorbent resin, 0.2 g, is uniformly put into a tea bag-like bag (40 mm × 150 mm) made by a nonwoven fabric, and soaked in a 0.9 weight % aqueous solution of sodium chloride. The teabag-like bag is taken out after 10 minutes and 30 minutes, respectively, and stood for draining for a designated time. Then, the weight is determined and the water absorption capacity is calculated by the following equation. Further, when only the tea bag being soaked, the weight obtained after water absorption is taken as a blank.

Water absorption capacity (g / g) = (weight of bag after absorption - blank) / (weight of water-absorption resin)

(3) Water Absorption Rate

To 20 mℓ of synthetic urine containing 1.9 weight % of urea, 0.8 weight % of sodium chloride, 0.1 weight % of calcium chloride, and 0.1 weight % of magnesium sulfate is added 1.0 g of a water-absorbent resin. The water absorption rate is defined with time passed until the water-absorbent resin absorbing the synthetic urine losts the flowing character of a swelling gel.

(4) Suction force

Water-absorbent resin, 1.0 g, is placed on a material containing synthetic urine, prepared by adding 20 mℓ of synthetic urine on a tissue paper of size 55 mm × 75 mm . After standing for 10 mm , a gel swelled is taken and weighed. The weight is defined as suction force of the resin from the tissue paper. At the same time, the presence of a fish-eye of the added water-absorbent resin was examined.

(5) Amount of Water-Soluble Component Eluted from Resin Surface

A disposable diaper for child composed of a nonwoven fabric, cotton-like pulp, a water-absorbent paper, and a waterproof film (having a weight of 72 g) is cut in half and 2.5 g of a polymer is uniformly scattered between the cotton-pulp and the water-absorbent paper and to this, 120 mℓ of the above-described synthetic urine is added, and the thus-prepared sample is stood for 16 hours at 37°C. After standing for 16 hours, the cotton-like pulp is only taken and a water-soluble component transferred from the pulp is extracted with 1,000 mℓ of pure water. This extract solution is filtered and a polymer component contained in this filtered solution is measured by using an acid-base titration method and thus, a total amount of a water-soluble component eluted is determined against the amount of water-absorbent resin as weight %.

Example 1

In a four-necked separable 2 L flask equipped with a stirrer, a reflux condenser, a thermometer, an inlet tube for nitrogen gas, and a dropping funnel was placed 1,000 mℓ of cyclohexane and dissolved 4.0 g of a sucrose fatty acid ester (DK-ESTER F-50, HLB = 6, a product from DAIICHI KOGYO SEIYAKU Co.,LTD.) and nitrogen gas was introduced into this solution to remove oxygen dissolved. In another flask containing a solution of 84.6 g of sodium acrylate, 21.6 g of acrylic acid, and 0.016 g of N,N'-methylene-bisacrylamide in 197 g of ion-exchanged water was dissolved 0.53 g of hydroxyethylcellulose (HEC-DAISERU EP-850, a product from DAISERU CHEMICAL Co.,LTD.) and was prepared a monomer solution adjusted at a monomer concentration of 35 weight % and viscosity of 40 cps. To this monomer solution was dissolved 0.15 g of potassium persulfate and then, nitrogen gas was introduced to remove oxygen dissolved in this aqueous solution.

Next, to the above separable flask solution was added the aqueous monomer solution in the latter flask and the mixture obtained was dispersed with stirring at 230 rpm. Then, polymerization reaction was initiated by raising bath temperature to 60 °C and completed by maintaining this temperature for 2 hours. After polymerization, the reaction mixture was treated by an azeotropic distillation with cyclohexane to remove water in the water-containing gel , filtered, and dried at 80°C under reduced pressure to obtain a polymer powder of sphere shape (A01). Water content for this polymer powder was 5.6 %.

With 100 weight parts (weight parts are hereinafter referred to as parts) of the polymer powder (A01) was mixed by a paddle type mixer a treatment solution composed of 0.3 parts of diethylene glycol, 4 parts of water, and 0.5 parts of isopropanol. When mixing, any large lump is not formed and all the composition passed through a 20 mesh metal net (mesh of 840 μm) when tried. The composition obtained was treated with heat by a paddle type dryer at 180 °C for 1 hour to obtain a water-absorbent resin (A11). Results obtained from properties measurements for this resin are shown in table 1.

Example 2

Except the use of 2.2 g of hydroxyethylcellulose (SP-600, a product from DAISERU CHEMICAL Co., LTD.), a polymerization reaction was carried out under the same conditions to those for example 1. Viscosity of the monomer aqueous solution was 800 cps and water content of a polymer powder of sphere shape (A02) was 6.8 % . With 100 parts of the polymer powder (A02) was mixed by a paddle type mixer a treatment solution composed of 0.1 parts of ethylene glycol diglycidyl ether, 3 parts of water, and 6 parts of methanol. When passing is tried, all the composition passed through a 20 mesh metal net. The composition obtained was treated with heat by a paddle type dryer at 100 °C for 1 hour to obtain a water-absorbent resin (A12). Results obtained from properties measurements for this resin

are shown in table 1.

Example 3

Except the use of 3.5 g of hexaglycerol-condensed ricinolate (STEP RP-6, a product from KAO Co., LTD.), a polymerization reaction was carried out in the same way as in example 1 to obtain a polymer powder of sphere shape (A03),which showed water content of 6.3 %. With 100 parts of the polymer powder (A03) was mixed by a V-type mixer a treatment solution composed of 0.08 parts of epichlorohydrin, 2 parts of water, and 4 parts of methanol. When tried, all the composition passed through a 20 mesh metal net and a lump is not observed which may be formed when mixing. The composion obtained was treated with heat by a paddle type dryer at 100 °C for 1 hour to obtain a water-absorbent resin (A13). Results obtained from properties measurements for this resin are shown in table 1.

Example 4

In a four-necked separable 2 L flask equipped with a stirrer, a reflux condenser, a thermometer, an inlet tube for nitrogen gas, and a dropping funnel was placed 1,000 mℓ of cyclohexane and dissolved 4.0 g of a sucrose fatty acid ester (DK-ESTER F-20, a product from DAIICHI KOGYO SEIYAKU Co., LTD.), and nitrogen gas was introduced into this solution to expel oxygen dissolved. In another flask 65.8 g of sodium acrylate, 21.6 g of acrylic acid, 0.076 g of polyethylene glycol diacylate (n = 14), and 15 g of sodium polyacrylate (AQUALIC OM-100, a product from NIPPON SHOKUBAI KAGAKU KOGYO Co., LTD., viscosity of 150 cps at 25°C for a 5 % aqueous solution) was dissolved in 250 g of ion-exchanged water to prepare an aqueous monomer solution of viscosity of 20 cps.

Next, into this solution, 0.12 g of sodium persulfate was dissolved and a reaction procedure was carried out in the same way as that for example 1 to obtain a polymer powder of sphere shape (A04), which showed water content of 4.8 %.

With 100 parts of the polymer powder (A04) was mixed by a paddle type mixer a treatment solution composed of 1 part of glycerol, 5 parts of water, and 1 part of isopropanol. All the composition passed through a 20 mesh metal net and any lump is not formed at the mixing. Then, the composition obtained was treated with heat by a paddle type dryer at 180 °C for 1.5 hours to obtain a water-absorbent resin (A14). Results obtained from properties measurements for this resin are shown in table 1.

Example 5

Except the use of sodium polyacrylate (AQUALIC FH, 2×10^4 cps at 25°C for viscosity of 1 % aqueous solution, a product from NIPPON SHOKUBAI KAGAKU KOGYO Co., LTD.) as a thickener, a reaction procedure was carried out in the same way as that for example 4 to obtain a polymer powder of sphere shape (A05), showing water content of 5.8 %. The viscosity of an aqueous monomer solution was 27 cps. With 100 parts of the polymer powder (A05) was mixed by a ribbon type mixer a treatment solution composed of 0.05 parts of glycerol glycidyl ether, 4 parts of water, and 0.8 parts of ethanol. All the composition passed through a 20 mesh metal net and, when mixing, any lump did not form. The composition obtained was treated with heat in a fluidized bed dryer at 100 °C for 1 hour to obtain a water-absorbent resin (A15). Results obtained from properties measurements for this resin are shown in table 1.

Example 6

Except that the amount of hydroxyethylcellulose (HEC-DAISERU EP-850, a product from DAISERU KAGAKU KOGYO Co., LTD.) in example 1 was changed into 1.6 g and the viscosity of aqueous monomer solution was adjusted at 2,000 cps, a polymerization reaction was carried out in the same way as that for example 1 to obtain 0.6 g of a water-absorbent polymer powder of all sphere shape (A06), which showed water content of 6.4 %. In the same way as carried out for example 1, this polymer powder (A06) was treated with a surface crosslinking to obtain a water-absorbent resin (A16). Results obtained from properties measurements for this resin are shown in table 1.

Example 7

Except that the amount of hydroxyethylcellulose (HEC-DAISERU SP-600, a product from DAISERU KAGAKU KOGYO Co.,LTD.) was 0.3 g and the viscosity of aqueous monomer solution was adjusted at 17 cps, a polymerization reaction was carried out in the same way as that for example 2 to obtain a water-absorbent polymer powder of sphere shape (A07) which showed water content of 5.9 %. In the same way as carried out for example 1, this polymer powder (A07) was treated with a surface crosslinking to obtain a water-absorbent resin (A17).

Results obtained from properties measurements for this resin are shown in table 1.

Example 8

Into 329 g of ion-exchanged water was dissolved 141 g of sodium acrylate, 36.1 g of acrylic acid, and 0.118 g of N,N'-methylen-bisacrylamide and, a static aqueous solution polymerization was carried out at 55 ~ 80 °C under a nitrogen atmospher by using 0.68 g of ammonium persulfate and 0.025 g of sodium hydrogensulfite to obtain a gel-like water-containing polymer, which was dried at 180 °C with a heated wind dryer, pulverized with a hammer-type pulverizer, and sieved with a 28 and a 60 mesh metal nets. The portion, which passed the 28 mesh net but not the 60 mesh net, was taken as a pulverized polymer powder (A010). Treatment of this polymer powder (A010) by surface crosslinking performed in the same way as that for examle 1 gave a water-absorbent resin (A110). Results obtained from properties measurements for this resin are shown in table 1.

Example for Comparison 1

Properties of the polymer powder (A01) obtained from example 1 were measured and summarized in table 1.

Example for Comparison 2

Except that 3.5 g of sorbitane monostearate (REODOL SP-S10, a product from KAO Co., LTD.) was used as a dispersing agent instead of a sucrose fatty acid ester, a polymerization procedure was carried out in the same way as for example 1 to obtain a polymer powder for comparison (B01), which had water content of 6.2 %. The polymer powder for comparison (B01) obtained was mixed with a liquid composition, which is the same as used for example 1, by a paddle type mixer. When mixing, were formed lumps in 8.6 %, which did not pass through a 20 mesh metal net. The composition obtained was treated with heat at 180 °C for 1 hour by using a paddle dryer to obtain a water-absorbent resin for comparison (B11). Results obtained from properties measurements for this resin are shown in table 1.

Example for comparison 3

Except no addition of hydroxyethylcellulose to a aqueous monomer solution, the same procedure as for example 1 was carried out to obtain a polymer powder (B02), which showed water content of 4.7 %. At this time, viscosity of a aqueous monomer solution was 7 cps.

The polymer powder for comparison (B02) was mixed by a paddle type mixer with a liquid compposition same as used in example 2. When mixing, were formed lumps in 8.2 % which did not pass through a 20 mesh metal net. The composition obtained was treated with heat by a fluidized bed dryer at 100 °C for 1 hour to obtain a water-absorbent resin for comparison (B12). Results obtained from properties measurements for this resin are shown in table 1.

Example for Comparison 4

Except that 4.0 g of tetraglycerol monostearate (POEMU J-4010, a product from RIKEN VITAMIN Co., LTD.) was used as a dispersing agent instead of a sucrose fatty acid ester used in example 1 and hydroxyethylcellulose was not added to the aqueous monomer solution, a procedure same as for example 1 was carried out to obtain a polymer powder (B03), which showed water content of 5.9 %.

The polymer powder for comparison (B03) was mixed with a liquid composition, which is the same as used for example 1, by a paddle type mixer. When mixing, were formed lumps in 7.6 % which did not pass through a 20 mesh metal net. The composition was treated with heat by a paddle dryer at 180 °C for 1 hour to obtain a water-absorbent resin for comparison (B13). Results obtained from properties measurements for this resin are shown in table 1.

Example for Comparison 5

In example 8, taking only a part passed through a 28 mesh metal net, a polymer powder for comparison (B04) was obtained. Treatment of this polymer powder for comparison (B04) with surface-crosslinkage gave a water-absorbent resin for comparison (B14). Results obtained from properties measurements for this resin are shown in table 1.

Table 1

	Water-absorbent resin obtained	Average particle diameter (μm)	Particle diameter distribution σ_{ζ}	Amount of lump (%)	Water absorption capacity (g/g) 10 min.	30 min.	Water absorption rate (sec.)	Suction force (g)	Formation of fish-eye *	Water-soluble component eluted (%)
Example 1	Water-absorbent resin (A11)	400	0.16	0	59	65	21	18.0	◎	0.15
Example 2	Water-absorbent resin (A12)	500	0.11	0	54	60	33	17.9	◎	0.08
Example 3	Water-absorbent resin (A13)	300	0.15	0	57	63	28	18.8	◎	0.12
Example 4	Water-absorbent resin (A14)	350	0.18	0	60	67	22	18.7	◎	0.07
Example 5	Water-absorbent resin (A15)	350	0.17	0	59	65	19	18.2	◎	0.05
Example 6	Water-absorbent resin (A16)	550	0.19	0	47	64	42	17.6	◎	0.09
Example 7	Water-absorbent resin (A17)	150	0.24	0	52	60	18	18.2	◎	0.13
Example 8	Water-absorbent resin (A110)	280	0.16	0	43	62	38	17.8	◎	1.82
Example for comparison 1	Polymer powder (A01)	400	0.16	—	44	62	65	13.2	○	4.2
Example for comparison 2	Water-absorbent resin for comparison (B11)	80	0.43	8.6	45	56	49	15.2	△	3.5
Example for comparison 3	Water-absorbent resin for comparison (B12)	100	0.41	6.2	41	53	45	15.1	△	3.1
Example for comparison 4	Water-absorbent resin for comparison (B13)	150	0.40	7.6	43	55	47	14.8	△	3.3
Example for comparison 5	Water-absorbent resin for comparison (B14)	230	0.58	3.5	38	59	47	15.0	△	5.1

(Note) * ◎: No formation of fish-eye at all. ○: Nearly no formation of fish-eye.
△: Some formation of fish-eye.

Claims

1. A water-absorbent resin comprising anionic group-containing polymer particles having an average particle diameter of 100-600 μm, showing particle diameter distribution of 0.35 or less in a value of logarithmic standard deviation, σ ζ, and being further treated with a cross-linking agent to provide crosslinking on th particl surface.

2. A method for producing a water-absorbent resin, said method comprising cross-linking the surface and neighbourhood of said surface of polymer powder particles having an average particle diameter in the range of 100-600 μm and a particle diameter distribution of 0.35 or less by logarithmic standard deviation (σ ζ), the polymer being obtained by polymerisation of an aqueous solution of an anionic water-soluble ethylenically unsaturated monomer wherein the crosslinking is obtained by treating the polymer with 0.005 - 20 wt.%, based on the polymer powder, of a cross-linking agent.

3. A method as claimed in claim 2 wherein the water content of said polymer powder is less than 10% by weight.

4. A method as claimed in claim 2 or 3 wherein the surface and neighbourhood of said surface is crosslinked by a cross-linking agent having two or more groups reactive to a functional group of the polymer powder.

5. A method as claimed in either one of claims 2, 3 or 4 wherein said polymer powder is produced by:

   (i) mixing an aqueous solution of an anionic water-soluble ethylenically unsaturated monomer having a viscosity of from 15 to 5000 cps as determined by a Brookfield rotational viscometer (25°C, 0.6 rpm) and being at least 20 weight % soluble in water, together with an inert hydrophobic organic solvent and a sucrose fatty acid ester and/or a polyglycerol fatty acid ester as a dispersing agent whereby said aqueous solution is dispersed and suspended in said inert hydrophobic organic solvent; and
   (ii) polymerising said monomer with a radical initiator.

6. A method as claimed in any one of claims 2 to 4 wherein said polymer powder is produced by:

   (i) drying a water-containing gel obtained by polymerizing an aqueous solution of an anionic water-soluble ethylenically unsaturated monomer; and
   (ii) pulverising and classifying said dried polymer.

7. A method as claimed in any one of claims 2 to 6 wherein the agent responsible for cross-linking the surface and neighbourhood of said surface is used in the form of a treatment solution with water and a hydrophilic organic solvent.

8. A method as claimed in claim 7 wherein said treatment solution comprises 0.005-20% crosslinking agent, 0.1-5% water and 0.01-6% hydrophilic organic solvent by weight relative to the polymer powder.

9. A method as claimed in any of claims 2 to 8 wherein said polymer powder is mixed with said treatment solution and then warmed at 40°C to 250°C.

Patentansprüche

1. Wasserabsorbierendes Harz, das eine anionische Gruppe aufweist, welche Polymerteilchen mit einem mittleren Teilchendurchmesser von 100 - 600 μm enthält, eine Teilchen-Durchmesserverteilung von 0.35 oder weniger gemäß einem Wert σ ζ der logarithmischen Standardabweichung ergibt und mit einem vernetzenden Wirkstoff weiter behandelt wird, um eine Vernetzung an der Teilchenoberfläche zu erhalten.

2. Verfahren zur Erzeugung eines wasserabsorbierenden Harzes, wobei das Verfahren aus einem Vernetzen der Oberfläche und der Nachbarschaft dieser Oberfläche von polymeren Pulverteilchen mit einem mittleren Teilchendurchmesser in dem Bereich von 100 - 600 μm und einer Teilchen-Durchmesserverteilung von 0.35 oder weniger gemäß der logarithmischen Standardabweichung σ ζ besteht und dabei das Polymer erhalten ist durch die Polymerisation einer wässrigen Lösung eines anionischen, wasserlöslichen, ethylenisch ungesättigten Monomers, wobei die Vernetzung erhalten wird durch die Behandlung des Polymers mit 0.005 - 20 Gew.-% auf der Basis des polymeren Pulvers eines vernetzenden Wirkstoffes.

3. Verfahren nach Anspruch 2, bei welchem der Wassergehalt des polymeren Pulvers weniger als 10 Gew.-% beträgt.

4. Verfahren nach Anspruch 2 oder 3, bei welchem die Oberfläche und die Nachbarschaft dieser Oberfläche durch einen vernetzenden Wirkstoff mit zwei oder mehr Gruppen vernetzt wird, die auf eine Funktionalgruppe des polymeren Pulvers reagieren.

5. Verfahren nach einem der Ansprüche 2, 3 oder 4, bei welchem das polymere Pulver hergestellt wird durch:

   (i) ein Mischen einer wässrigen Lösung eines anionischen, wasserlöslichen, ethylenisch ungesättigten Monomers mit einer Viskosität von 15 bis 5.000 cps gemäß der Bestimmung durch ein Brookfield-Rotationsviskosimeter (25°C, 0.6 U/min) und zu wenigstens 20 Gew.-% in Wasser löslich, zusammen mit einem inerten hydrophoben organischen Lösungsmittel und einem Sucrose-Fettsäureester und/oder einem Polyglycerol-Fettsäureester als einem Dispersionswirkstoff, wodurch die wässrige Lösung dispergiert und in dem inerten hydrophoben organischen Lösungsmittel suspendiert wird; und

   (ii) ein Polymerisieren des Monomers mit einem Radikalinitiator.

6. Verfahren nach einem der Ansprüche 2 bis 4, bei welchem das polymere Pulver hergestellt wird durch:

   (i) ein Trocknen eines Wasser enthaltenden Gels, das durch ein Polymerisieren einer wässrigen Lösung eines anionischen, wasserlöslichen, ethylenisch ungesättigten Monomers erhalten ist; und

   (ii) ein Pulverisieren und Klassifizieren des getrockneten Polymers.

7. Verfahren nach einem der Ansprüche 2 bis 6, bei welchem der für ein Vernetzen der Oberfläche und der Nachbarschaft dieser Oberfläche verantwortliche Wirkstoff in der Form einer Behandlungslösung mit Wasser und einem hydrophilen organischen Lösungsmittel benützt wird.

8. Verfahren nach Anspruch 7, bei welchem die Behandlungslösung aus 0.005 bis 20 % des vernetzenden Wirkstoffes, 0.1 bis 5 % Wasser und 0.01 bis 6 % des hydrophilen organischen Lösungsmittels in Gewichtsmengen relativ zu dem polymeren Pulver besteht.

9. Verfahren nach einem der Ansprüche 2 bis 8, bei welchem das polymere Pulver mit der Behandlungslösung vermischt und dann auf 40°C bis 250°C erwärmt wird.

Revendications

1. Résine absorbant l'eau comprenant des particules d'un polymère contenant un groupement anionique dont le diamètre moyen est compris ente 100 et 600 micromètres, dont la distribution du diamètre est de 0,35 ou moins, selon une valeur de déviation standard logarithmique $\sigma \zeta$, lesdites particules étant ensuite traitées avec un agent réticulant afin de permettre la réticulation de leur surface.

2. Procédé pour la fabrication de résines absorbant l'eau, ledit procédé comprenant la réticulation de la surface et du voisinage de ladite surface des particules de poudre de polymère, dont le diamètre moyen est compris entre 100 et 600 micromètres, et dont la distribution du diamètre est de 0.35 ou moins selon une déviation standard logarithmique ($\sigma \zeta$), le polymère étant obtenu par polymérisation d'une solution aqueuse d'un monomère anionique éthylénique insaturé soluble dans l'eau, dans lequel la réticulation est obtenue par traitement du polymère avec de 0,005 à 20 % d'un agent réticulant, en poids de la poudre de polymère.

3. Procédé selon la revendication 2, dans lequel la teneur en eau de ladite poudre de polymère est inférieure à 10 % en poids.

4. Procédé selon l'une des revendications 2 ou 3, dans lequel la surface et le voisinage de ladite surface est réticulé par un agent réticulant ayant deux ou plusieurs groupes réactifs vis-à-vis d'un groupe fonctionnel de la poudre de polymère.

5. Procédé selon l'une des revendications 2, 3 ou 4, dans lequel la fabrication de ladite poudre de polymère consiste :

- a mélanger une solution aqueuse d'un monomère anionique ethylenique insaturée soluble dans l'eau présentant une viscosité comprise entre 15 et 5000 cps, déterminée par un viscosimètre rotatif Brookfield (25°C, 0,6 tpm), et dont la solubilité dans l'eau est d'au moins 20% en poids avec un solvant organique inerte hydrophobe et un ester d'acide gras et de saccharose et/ou un ester d'acide gras et d polyglycérol utilisé en tant qu'agent dispersant, afin que ladite solution aqueuse soit dispersée et mise en suspension dans ledit solvant organique inerte hydrophobe et ;
- à polymériser ledit monomère avec un initiateur radicalaire.

6. Procédé selon l'une des revendications 2 à 4 dans lequel la fabrication de ladite poudre de polymère consiste:

- à sécher un gel contenant de l'eau, obtenu par polymérisation d'une solution aqueuse d'un monomère anionique éthylénique insaturé soluble dans l'eau et;
- à pulvériser et classer le polymère séché.

7. Procédé selon l'une des revendications 2 à 6, dans lequel l'agent de réticulation de la surface et du voisinage de la surface, est utilisé sous forme d'une solution de traitement avec de l'eau et un solvant organique hydrophile.

8. Procédé selon la revendication 7, dans lequel la solution de traitement comprend de 0,005 à 20 % d'agent réticulant, de 0,1 à 5 % d'eau, et de 0,01 à 6 % de solvant organique hydrophile en poids par rapport au poids de la poudre de polymère.

9. Procédé selon l'une des revendications 2 à 8, dans lequel ladite poudre de polymère est mélangée avec ladite solution de taitement, et est ensuite chauffée à une température comprise entre 40°C et 250°C.

Fig.1

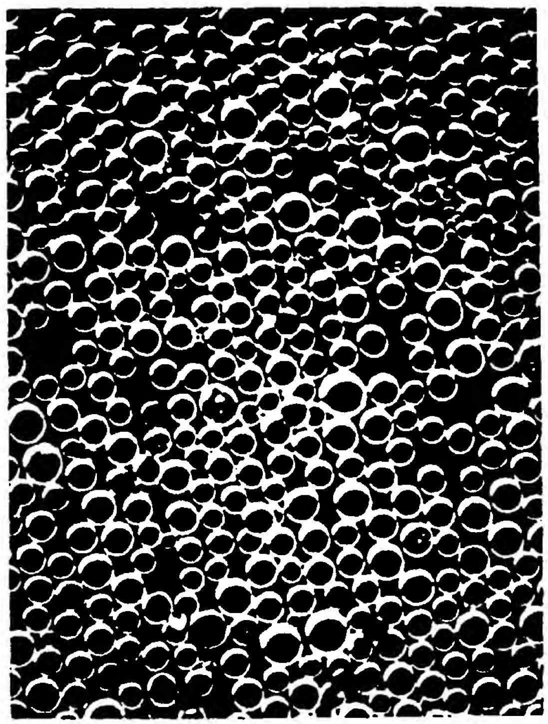

Fig. 2